

*RISK ANALYSES FOR
DISPOSING
NONHAZARDOUS OIL FIELD
WASTES IN SALT CAVERNS*

**Prepared for: U.S. Department of Energy
Office of Fossil Energy
Under Contract W-31-109-ENG-38**

**Prepared by: David Tomasko, Deborah Elcock, John Veil,
and Dan Caudle
Argonne National Laboratory
Argonne, IL**



19980127 020

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

DTIC QUALITY INSPECTED 3

December 1997

AQ
or

New Text Document.txt

26 January 1998

This paper was downloaded from the Internet.

Distribution Statement A: Approved for public release;
distribution is unlimited.

POC: Department of Energy
Date: December 1997

Acknowledgments	iv
1. Introduction	4
2. Salt Cavern Background	6
2.1 Origins and Development	6
2.2 Waste Disposal in Caverns	8
2.3 Post-Closure Cavern Behavior	9
2.4 Cavern Release Scenarios	10
3. Contaminants of Potential Concern	12
4. Fate and Transport for Contaminants of Potential Concern	14
4.1 Benzene	14
4.2 Lead	15
4.3 Arsenic	15
4.4 Cadmium	16
4.5 Chromium	16
4.6 Boron	17
5. Hydrogeology	18
5.1 Gulf Coast Hydrogeology	18
5.2 Texas and New Mexico Hydrogeology	18
6. Release Calculations	20
6.1 Initial Concentrations for Contaminants Released from a Cavern	20
6.2 Cavern Release Scenarios	22
6.2.1 Inadvertent Intrusion	22
6.2.2 Release through the Cavern Seal	23
6.2.3 Release of Contaminated Fluid through Cracks	26
6.2.4 Release of Contaminated Fluid through Leaky Interbeds or Nonhomogeneous Zones	27
6.2.5 Partial Cavern Roof Fall	28
6.2.6 Probabilities of Occurrence	28
7. Toxicity of Contaminants of Potential Concern	30
7.1 Hazard Identification	30
7.2 Dose-Response Relationships for Contaminants of Concern	32
7.2.1 Slope Factors	32
7.2.2 Reference Doses	32
8. Risk Characterization	34
8.1 Exposure Scenarios	34

8.2 Cancer Risks	35
8.3 Noncancer Risks	36
9. Sensitivity of Risks to Operating Procedures and Regulatory Structures	38
10. Summary	39
11. References	40
Tables	47

Acknowledgments

The authors wish to express their appreciation to those individuals who gave their time to review the draft version of this report and provide us with comments. In particular we thank H.W. Diamond of the Solution Mining Research Institute, who coordinated an extensive review of the draft report. The review panel consisted of the following persons:

Pierre Berest	Ecole Polytechnique
Benoit Brouard	Ecole Polytechnique
Ph. Cosenza	Ecole Polytechnique
Dennis Crist	Ohio Department of Natural Resources
Fritz Crotogino	Kavernen Bau- und Betriebs GmbH
Ken E. Davis	Envirocorp Services & Technology, Inc.
Anna Dombrowski	Envirocorp Services & Technology, Inc.
H.W. Diamond	Solution Mining Research Institute
Norbert Heitmann	PB-KBB, Inc.
Gordon Kiddoo	consultant
James Linn	Sandia National Laboratories
Jeff McCartney	Texas Brine Corp.
James Oswald	Morton Salt
Joe L. Ratigan	RE/SPEC, Inc.
Robert Thoms	AGM, Inc.

Additional comments were received separately from the following persons:

Richard Ginn	Railroad Commission of Texas
Susan Hovorka	Texas Bureau of Economic Geology

The final report reflects the contributions of each of these persons.

We also wish to thank Nancy Johnson of the Office of Fossil Energy at DOE headquarters and John Ford of DOE's National Petroleum Technology Office for their continued encouragement and support of our salt cavern research program.

Risk Analyses for Disposing Nonhazardous Oil Field Wastes in Salt Caverns

D. Tomasko, D. Elcock, J. Veil, and D. Caudle

Executive Summary

Salt caverns have been used for several decades to store various hydrocarbon products. In the past few years, four facilities in the United States have been permitted to dispose nonhazardous oil field wastes in salt caverns. Several other disposal caverns have been permitted in Canada and in Europe. This report evaluates the possibility that adverse human health effects (carcinogenic and noncarcinogenic) could result from exposure to contaminants released from the caverns in domal salt formations used for nonhazardous oil field waste disposal. The evaluation assumes normal operations but considers the possibility of leaks in cavern seals and cavern walls during the post-closure phase of operation. In this assessment, several steps were followed to identify possible human health risks. At the broadest level, these steps include identifying a reasonable set of contaminants of possible concern, identifying how humans could be exposed to these contaminants, assessing the toxicities of these contaminants, estimating their intakes, and characterizing their associated human health risks.

The contaminants of concern for the assessment are benzene, cadmium, arsenic, and chromium. These were selected as being components of oil field waste and having a likelihood to remain in solution for a long enough time to reach a human receptor.

Post-closure releases of fluids from the caverns can be classified under the following scenarios for the present study: inadvertent intrusion by unintentionally drilling a new well into a closed cavern; failure of the cavern seal due to increased pressure from salt creep and geothermal heating; release of contaminated fluid through cracks, leaky interbeds, or nonhomogeneous zones composed of higher permeability material; and partial cavern roof fall. Most releases would be to deep aquifers at or near the top of the cavern, although under several scenarios, released contaminants can move upward through the well casing and leak out into shallow aquifers.

For the inadvertent intrusion scenario, up to 2,000 gallons (gal) of contaminated fluids would move quickly to the surface where, if not contained by the drilling blowout-prevention system, would most likely form a pool on the ground surface. These materials would not penetrate very far into the ground and could be readily cleaned up. Because the volume of released fluid for this scenario would be small, the effects would be of very short duration, the liquid would not be potable, and such a spill would be quickly remediated, the scenario was eliminated from further analyses.

In most of the other scenarios, the release pattern would be to have the pressure build up in the cavern to a level that causes seal failure or cracks. A small amount of contaminated fluids (assumed to be 2,000 gal) would be released and the internal cavern pressure would decrease. The cracks or leaks could self-heal after the release because of additional salt creep. With repressurization of the cavern, the cracks or leaks could once again open, producing a series of short contaminant pulses (probably on the order of hours to days in duration). Under the remaining scenarios, releases would be gradual and long-term seeps through cracks, leaky interbeds, or other nonhomogeneous zones composed of higher permeability material.

Not every closed cavern is expected to undergo releases, so some measure of the probability of failure must be incorporated into the analyses. Because experience with disposal caverns is limited and they have not been in operation for very many years, virtually no information exists about the accident or release rates from disposal caverns. In order to estimate the range of the probabilities of occurrence, a questionnaire was distributed to experts in the field of salt caverns. The panel of experts was asked to provide both a "best-estimate" and a "worst-case" estimate of the probability of occurrence for each of the release scenarios. The estimates from each expert were averaged. Averaged best-estimates for the different scenarios ranged from 0.006 for partial roof fall plus cavern seal failure and fluid release at shallow depth to 0.1 for partial roof fall plus fluid release at depth. Averaged worst-case estimates ranged from 0.04 for seal failure with fluid release at shallow depth to 0.29 for partial roof fall plus fluid release at depth.

Once contaminated fluids leave the cavern, they are expected to migrate laterally and vertically through different formations and aquifers. During the time the fluids travel from the point of release to the receptor site (assumed to be 1,000 ft laterally from the cavern) various physical, chemical, and biological processes occur that reduce the concentration of the contaminants. Fate and transport modeling was used estimate the contaminant concentrations at the receptor point (exposure point concentrations).

Risk calculations were conducted using the exposure point concentrations, assumed drinking water intake rates, and standard assumptions regarding exposure time, duration, and frequency. Based on assumptions that were developed for a generic cavern and generic oil field wastes, the estimated human health risks for worst-case conditions are very low (excess cancer risks of between 1.1×10^{-8} and 2.0×10^{-17}) and hazard indices (referring to noncancer health effects) of between 6×10^{-5} and 1.0×10^{-7} . Normally, risk managers consider risks of 1×10^{-6} and less and hazard indices of less than 1 to be acceptable. For best-estimate conditions, the excess cancer risks were calculated to be between 1.3×10^{-9} and 3.8×10^{-18} and the hazard indices were between 1.4×10^{-5} and 1.9×10^{-8} .

Caveats regarding the use of the results of this report include the following. First, the assessment does not address risks to workers at the cavern disposal site. Such risks would be comparable to or less than worker risks associated with hydrocarbon cavern storage operations. Second, the assessment does not determine whether any health effects will occur in the future; it only estimates cancer risk and potential for noncarcinogenic effects. Third, risks have only been

estimated for contaminants for which toxicity values were available; just because there is no toxicity value does not mean there is no risk. Finally, the assessment is limited to human health effects produced by nonradioactive contamination; it does not address the possible ecological risks associated with salt cavern disposal, nor does it estimate risks associated with NORM that may be included in oil field wastes.

1. Introduction

In 1996, the U.S. Department of Energy (DOE), Office of Fossil Energy, asked Argonne National Laboratory (ANL) to conduct a preliminary technical and legal evaluation of disposing of nonhazardous oil field wastes (NOW) into salt caverns. The conclusions of that study, based on preliminary research, were that disposal of oil field wastes into salt caverns is feasible and legal. If caverns are sited and designed well, operated carefully, closed properly, and monitored routinely, they can be a suitable means for disposing of oil field waste (Veil et al. 1996). Considering these findings and the increased U.S. interest in using salt caverns for nonhazardous oil field waste disposal, the Office of Fossil Energy asked ANL to conduct a preliminary identification and investigation of the risks associated with such disposal.

The purpose of this report is to evaluate the possibility that adverse human health effects (carcinogenic and noncarcinogenic) could result from exposure to contaminants released from the caverns in domal salt formations used for nonhazardous oil field waste disposal. The evaluation assumes normal operations but considers the possibility of leaks in cavern seals and cavern walls during the post-closure phase of operation. It does not consider the risks associated with emissions from surface equipment operating at the site, nor does it consider the risks associated with surface oil leaks or other equipment-related spills or accidents.

The study focuses on possible long-term risks to human health. It does not address potential ecological effects, although such effects could result. Also, risks associated with naturally occurring radioactive materials (NORM) are not addressed. This preliminary assessment estimates risks associated with disposal in a single generic cavern only. No attempt has been made to address the possibility or likelihood that several caverns may be located in relatively close proximity and that more than one cavern could be a source of contamination to a given receptor. Also, no attempt has been made to evaluate the possible impacts of synergistic effects of multiple contaminants on a single receptor.

Because the history of salt cavern use for solid waste disposal is very limited, no readily available data could be accessed for this study. As a result, data from similar operations and professional judgment were used to develop the possible release mechanisms assumed in this hypothetical, generic analysis. The validity of the results would be enhanced if real data could be used. As data are generated on the use and post-closure operations of salt caverns used for solid waste disposal, they should be incorporated to update this study.

In this assessment, several steps were followed to identify possible human health risks. At the broadest level, these steps include identifying a reasonable set of contaminants of possible concern, identifying how humans could be exposed to these contaminants, assessing the toxicities of these contaminants, estimating their intakes, and characterizing their associated human health risks. The risk assessment methodology and techniques used in this report are based in large part on two documents. The first document is a training manual that was developed for a risk assessment workshop sponsored by DOE (DOE 1996). The second is the Risk Assessment Guidance for Superfund (U.S. Environmental Protection Agency [EPA] 1989).

The remainder of this report consists of nine sections. Section 2 provides background on the development, use, and closure of salt caverns that may be used for disposal of nonhazardous oil field wastes and possible cavern release scenarios. Section 3 identifies contaminants of potential concern that could cause harm to human health. Sections 4, 5, and 6 provide information for assessing potential exposure pathways that the contaminants of concern could take to reach human populations. Specifically, Section 4 describes fate and transport mechanisms of the contaminants of concern; Section 5 describes specific hydrogeologic conditions of locations where salt caverns are most likely to be used for oil field disposal (Gulf Coast, Texas, and New Mexico); and Section 6 describes potential release modes that could cause contaminants to leak from the cavern and be transported to areas where human populations may be exposed. Section 6 also estimates possible concentrations of the contaminants to which humans could be exposed under various release scenarios. Section 7 describes the toxicity of those contaminants that could come in contact with humans, given the fate and transport mechanisms identified in Section 5 combined with the potential exposure pathways described in Section 6. Section 8 estimates the potential intakes of those contaminants by humans and characterizes the risks to which those humans may be subjected on the basis of the intake of the contaminants (the potential for harm), their toxicities, and the release assumptions. Section 9 addresses the sensitivity of the estimated risks to operating procedures and potential regulatory structures, and Section 10 summarizes the results of the analyses.

2. Salt Cavern Background

The following section discusses the origins and development of salt caverns in the United States, waste disposal in caverns, sealing and abandoning salt caverns, and scenarios under which cavern contents could leave the cavern.

2.1 Origins and Development

As discussed in Veil et al. (1996), subsurface salt deposits occur in two major forms in the United States: bedded salt and salt domes. Although salt deposits occur in many parts of the United States, the occurrence of salt in quantities and locations that would promote commercial development is limited. There are 16 states in which salt occurs in sufficient quantity to be mined by either excavation or solution mining or to be recovered through solar evaporation. States having major salt deposits are Alabama, Arizona, Colorado, Kansas, Louisiana, Michigan, Mississippi, Montana, New Mexico, New York, North Dakota, Ohio, Oklahoma, Pennsylvania, Texas, and Utah. Of these states, those with the most significant salt mining are Kansas, Louisiana, Michigan, New Mexico, New York, Ohio, and Texas (Veil et al. 1996).

Bedded salt formations occur in layers interspersed with such sedimentary materials as anhydrite, shale, dolomite, and other more soluble salts (e.g., potassium chloride). These materials have varying degrees of permeability, but all are generally low (Freeze and Cherry 1979). The bedded salt deposits are tabular and can contain significant quantities of impurities.

Salt domes are large, nearly homogeneous formations of sodium chloride, although they may contain nonhomogeneous zones. Pfeifle et al. (1995) report that the typical anhydrite (CaSO_4) content of Gulf Coast salt domes averages less than 5%. These domes were created by geological processes that spanned millions of years (Chilingarian et al. 1989). About 30 million years ago, salt buried by more dense materials flowed to form pillows. Because of its lower density, salt flowed upward to form diapirs (domes or anticlinal folds whose overlying rocks have been ruptured by the squeezing-up of the more plastic salt core) and piercing overlying units.

As the salt passed up through the overlying sediments, long, finger-like projections developed. The depth of the intruded salt (sedimentary piercements) can be greater than 10,000 ft (Whiting 1981a), and the top width of the salt domes ranges from about 0.5 to 2.5 miles (Chilingarian et al. 1989). If the intruded salt contacted undersaturated water, dissolution would occur. Through a complex interaction of dissolution, recrystallization, hydration of anhydrite to form gypsum, sulfate reduction, cementation, etc., a caprock was often formed. Although caprocks are common in the vicinity of salt domes, they do not always exist there (Linn 1997).

At the top of the caprock, a region of limestone frequently developed. This limestone may have been formed by a number of processes, including reduction of the calcium-sulfate caprock, and precipitation from calcium-sulfate-rich water (Werner 1986).

As the salt intruded the Cenozoic sediments along the Gulf Coast, various minerals were often precipitated in the vicinity of the caprock. Along with the minerals, oil was frequently trapped under the edge of the caprock. Because of the high probability of finding oil and other valuable minerals, salt domes have been extensively explored and mined for more than 100 years.

Starting in the late 1800s, salt domes were commercially mined for salt by using various leaching techniques. The shapes of the resulting caverns were often irregular because of the techniques applied, but a number of caverns, such as West Hackberry Cavern 11, are nearly symmetrical (Tomasko 1985).

Salt caverns are used for storing hydrocarbons. The earliest cavern storage in salt domes for liquified petroleum gas (LPG) started in 1951; LPG storage in bedded salt started somewhat sooner, in the early 1940s (Querio 1980). Some of the liquified products stored include propane, butane, ethane, fuel oil, gas, and crude oil.

DOE acquired the rights to some existing caverns for the Early Storage Reserve (ESR) of the Strategic Petroleum Reserve (SPR). The ESR was designed to store 250 million barrels of oil of which about two thirds were to be placed in solution-mined caverns and one third in a conventional rock salt mine. Acquisitions for the ESR were made about 1977. SPR now has a capacity of 680 million barrels, and the rock salt mine has been removed from the program (SMRI 1997).

Private industry in the United States operates a large number of caverns for storing liquid petroleum products, petrochemicals, and natural gas. European countries have also used salt caverns as containment sites for the disposal of drilling muds and cuttings from deep oil and gas wells (Testa 1994).

Nearly all salt caverns in the SPR are 2,000 ft tall and have a cavern roof that is at a depth of about 2,000 ft. The diameters of the caverns vary greatly, but a typical value is about 300 ft (Biringer 1984). The distance between caverns is variable, but a typical separation distance from center-to-center is more than 600 ft (Whiting 1981b). Volumetrically, SPR caverns are large, and each cavern contains about 10 million barrels (420 million gallons) of crude oil. Private sector caverns are generally smaller than the SPR caverns and have various sizes, shapes, and depths (Hickerson 1995).

To create salt caverns, water that is not fully salt-saturated is injected into a salt stock and the resulting brine solution is withdrawn. This method is referred to as solution mining (Testa 1994). The development and shape of the salt cavern can be controlled by the method used for construction. In the direct circulation method, fresh water is injected through a tubing string from the surface, and brine is withdrawn through an annular space between the tubing and final casing. In the reverse circulation method, fresh water enters through the annulus, and brine is removed through the tubing string. A combination of these two methods, or other more complicated methods, can be used to obtain the desired cavern shape. The American Petroleum Institute (API) provides illustrations and more details on these methods (API 1994).

2.2 Waste Disposal in Caverns

Use of salt caverns for waste disposal in the United States has been limited. A summary of current disposal practices is given in Veil et al. (1996) along with a discussion on using caverns for waste disposal in Canada, the United Kingdom, Germany, the Netherlands, and Mexico.

In this study, we consider the disposal of nonhazardous oil field wastes in salt caverns. As discussed in Section 3, the majority of material disposed of would be tank bottom wastes (waste material from washing tanks, heater tanks, and stock tanks). This solid or sludge-like waste consists of accumulated heavy hydrocarbons, paraffins, inorganic solids, and heavy emulsions (EPA 1994b). Physically, the waste consists of approximately 50% water, 15% clay, 10% scale, 10% corrosion products, 10% oil, and 5% sand. Its specific gravity ranges from about 1.5 to 2.0. The principal contaminants of concern in the waste include benzene, lead, arsenic, cadmium, chromium, and boron (see Section 3).

Initially, the caverns would be filled with brine. Wastes would then be introduced as a slurry of waste and a fluid carrier (brine or fresh water). Three scenarios are possible for introducing the waste material: (1) the waste can be pumped down tubing to the bottom of the cavern and the displaced brine can be withdrawn through an annulus; (2) the waste can be pumped down an annulus and the displaced brine can be withdrawn through the tubing; and (3) the waste can be injected through one well and the brine withdrawn from another well. The first scenario is the most likely method because of associated costs and ease of use (Veil et al. 1996).

As the slurry is injected, the cavern acts as an oil/water/solids separator. The heavier solids sink to the bottom of the cavern and form a pile. Any free oils and hydrocarbons float to the top of the cavern, because they are less dense than water. An organic blanket could be injected into the cavern to prevent additional leaching of the cavern's roof by water that is not fully saturated with salt. Clays in the slurry can mix with the brine, forming a suspension above a brine/waste interface. Clean brine displaced by the incoming slurry would be removed from the cavern and either sold as a product or disposed of in an injection well.

Early in the life of the disposal cavern, clean brine is withdrawn from hundreds of feet above the surface of the waste pile or interface. As the cavern fills, the brine becomes dirtier (i.e., it will have a higher clay and oil content). This dirty brine can produce operational difficulties (e.g., clogging of pumps) and additional expenses (Veil et al. 1996). The cavern is considered to be "full" of waste when disposed material being returned with the displaced fluid becomes a problem. When the cavern is full, the operator seals the cavern.

2.3 Post-Closure Cavern Behavior

Once the cavern has been filled with waste, the cavern would be sealed and the borehole plugged with cement. Bridge plugs would be placed in the well bore above and below water-

bearing intervals to isolate these intervals permanently. This procedure is often used in the oil and gas industry to abandon wells.

A waste-filled cavern that has been sealed is subject to a number of complex physical processes: reduction in cavern volume caused by salt creep (the process by which salt surrounding the cavern flows into the cavern space as a pseudo-fluid [Bishop 1986, Freeze et al. 1995]); convective mixing in the upper, brine-filled portion of the cavern; differential settling and compaction of solids; chemical reaction and compaction of the waste material; and an increase in pressure produced by the combined effects of salt creep and the addition of sensible heat (heat derived from the geothermal gradient vertically across the cavern — approximately 13 °F per 1,000 ft at a depth of 1,000 ft [Tomasko 1985]);

During a transient period of several years after closure of a cavern filled with brine, pressure can exceed the lithostatic value (pressure in surrounding salt) because of thermal expansion of the brine. The amount of over-pressurization is a function of cavern size (Berest and Brouard 1995). Similarly, cavern pressure can exceed the lithostatic value after a longer time period when, due to salt creep, brine pressure will balance average lithostatic pressure, resulting in a slight excess of brine pressure at the top of the cavern (Langer et al. 1984; Wallner 1986). This occurs because lithostatic pressure increases linearly with depth, while brine pressure is constant within the cavern.

The presence of a small quantity of gas in the sealed cavern can mitigate the effects of pressure buildup because the gas drastically increases the cavern compressibility or decreases the cavern stiffness (Berest et al. 1997a). Gases can be produced in a sealed disposal cavern in a number of ways, including bacterial degradation of the waste, corrosion, and natural releases from the salt formation itself (e.g., carbon dioxide, hydrogen sulfide, hydrogen, methane, etc.). Bacterial degradation of organic material in the waste can generate such gases as carbon dioxide, hydrogen sulfide, and methane. However, for several reasons, bacterial action would not generate a large quantity of gas. For example, because many bacteria have a limited tolerance for salt, conditions in the cavern would not be conducive for bacterial growth and reproduction (Stanier et al. 1963; and Postgate 1965). Even if the bacteria could survive in brine, there are other natural curbs on their activity. For aerobic bacteria, the supply of oxygen would be limited (only 8 parts per million [ppm] of oxygen are in the fresh water that is in contact with air at 25°C). For anaerobic conditions, bacteria could produce hydrogen sulfide gas if the waste contains sulfate. The hydrogen sulfide produced would, however, be water soluble and would dissolve in the brine. As the pressure in the cavern increased with time, the solubility of the hydrogen sulfide would also increase and minimize free-gas production.

Metal components of the waste material could corrode and generate hydrogen gas, especially at low pH conditions (acid environment). Such processes are common causes for equipment failures in oil and gas production systems. In a waste cavern, pH would be controlled by the partial pressure of carbon dioxide. Ambient carbon dioxide levels in the cavern would not

support a significant corrosion rate, and hydrogen gas would not be generated. The only other source of acid in oil field waste would be spent acid from well stimulations (Bradley 1992). If the pH of such wastes is adjusted to six or above prior to disposal, no significant gas production would occur. Because the principal waste material for this study is tank bottom material and not spent acids, little acid would be present and the production of hydrogen gas would be negligible.

Gas production in caverns is also controlled by pressure effects. As the pressure in a cavern builds up, the gas production rates would fall correspondingly. This process would limit the volume of any gases produced.

A recent study of the behavior of brine-filled, sealed caverns suggests that the permeability of the material surrounding the cavern can also influence pressure buildup (Wallner and Paar 1997). Because of a very slow pressure increase within a sealed salt cavern, the pressure at the top of the cavern would only exceed the lithostatic value after a long time (on the order of thousands of years for a 1,000-ft tall cavern). Because the rock salt formation becomes permeable if the fluid pressure exceeds the stress in the salt, small leakage rates of fluids from the top of the cavern are predicted. This leakage would compensate for the overpressurization at the top of the cavern and return the system to an equilibrium condition.

Details on the pressurization of a sealed cavern that is filled with NOW are currently unavailable, although the behavior is expected to be similar to that discussed above with the exception that the compressibility of the wastes may alter the time scale and magnitude of the system response. More study of actual waste disposal caverns would help to clarify this issue.

2.4 Cavern Release Scenarios

In assessing risks to the public from disposing of NOW in caverns, potential release modes must be determined. At the present time, there is little information on accidents for cavern disposal systems because there are only a few disposal caverns in operation and they have not been operating for very many years. However, what little accident information exists from disposal and storage caverns indicates that the caverns are safe and that the only accidents that have occurred were associated with surface facilities. Because insufficient information exists for quantifying release probabilities for cavern disposal, results from the liquid petroleum gas (LPG) storage industry and the Strategic Petroleum Reserve (SPR) are used in this study as a basis for identifying potential release scenarios.

Although LPG industries and the SPR have a long history of safe operations, a statistically meaningful data base for risk analysis is absent. To overcome this difficulty, a subjective, semiquantitative methodology was developed by Radian Corporation to evaluate risks for the LPG industry (Radian Corporation 1995). This methodology, developed by a panel of experts in the field of salt-cavern conversion for LPG storage, was based on a modified-Delphi approach (Brown and Helmer 1964) in which variability of the estimated parameters are reduced through group interaction.

The Radian study identified 22 accident scenarios that could lead to releases to the environment. These accident scenarios can be grouped into three general categories: (1) cavern development and conversion, (2) cavern filling, and (3) post-closure releases. In this study, impacts were analyzed for only the last of the accident scenarios identified, post-closure releases. Impacts from the first two scenarios are better addressed in a second tier assessment, in which site-specific information would be used and more detailed design parameters would be defined.

Post-closure releases can be classified under the following categories for the present study: inadvertent intrusion; failure of the cavern seal; release of contaminated fluid through cracks, leaky interbeds, or nonhomogeneous zones composed of higher permeability material; and partial cavern roof fall.

3. Contaminants of Potential Concern

In a standard risk assessment, the first step is collecting and evaluating data. One result of the data collection exercise is the identification of contaminants of potential concern. Contaminants of potential concern at a site are those that may be hazardous to human health and/or the environment under current or future site conditions. Selecting contaminants of potential concern helps focus the risk assessment on those contaminants that may be of potential significance to human health.

It is important to select contaminants of potential concern for several reasons. If all possible contaminants were considered, the risks associated with naturally occurring contaminants could drive the assessment. For example, high background levels of particular contaminants, such as manganese, could obscure risks related to oil field wastes. Also, the level of effort and the cost of analysis increase with the number of contaminants being evaluated. Probably hundreds of contaminants associated with nonhazardous oil field wastes could be identified, depending on the types of crude that were produced, the types of drilling muds used, and the geochemistry of the formation from which the oils were extracted.

As the risk assessment is conducted, it may be determined that the risks associated with some potential contaminants are insignificant and can be dropped from further consideration. For example, the ability of some potential contaminants to be transported may be insufficient to allow them to come in contact with humans. In such cases, the contaminant would not be considered further in the risk assessment.

The term nonhazardous oil-field waste should not be interpreted to mean that no hazardous substances are found in oil-field wastes. In 1988, EPA made a determination that exempted wastes from the exploration, development, and production of crude oil, natural gas, and geothermal energy from regulation as hazardous under Subtitle C of the Resource Conservation and Recovery Act (RCRA). In 1993, EPA added many other wastes that were uniquely associated with exploration and production operations to those already exempted from RCRA Subtitle C requirements. Thus, exempt wastes include drilling fluids, produced water, and other wastes associated with the exploration, development, or production of crude oil, natural gas, or geothermal energy. However, even though a waste is exempted from Subtitle C requirements, it may still contain hazardous contaminants. In its regulatory determination, EPA concluded that the wastes exempted from regulation under Subtitle C could be better controlled through improvements to existing state and Federal regulatory programs.

The current study is a preliminary, generic risk assessment; collecting the primary data needed to identify contaminants of potential concern is beyond its intended scope. Rather, results of the analysis presented in EPA's 1987 Report to Congress (EPA 1987) and a later draft pertaining to Selected Associated Wastes (EPA 1994b) were used to identify contaminants of potential concern.

As described in its Report to Congress, EPA used waste sampling and analysis data to characterize drilling wastes and produced water for quantitative risk modeling. Limited available data prohibited the EPA from developing separate waste-stream characterizations for various geographic zones; as a result, one set of waste characteristics was used to represent the nation. The major factors EPA used in selecting contaminants of concern were (1) median and maximum concentrations in the waste samples, (2) frequency of detection in the waste samples, (3) mobility in groundwater, and (4) concentrations at which human health effects, aquatic toxicity, or resource damage start to occur. By using this screening process, EPA selected several chemicals considered likely to dominate risk estimates. These chemicals included arsenic, benzene, boron, cadmium, and chromium (VI).

The 1987 Report to Congress focused primarily on produced water and drilling muds. Because the EPA estimated that these two types of waste constituted over 98% of the industry waste stream in 1988, the EPA began evaluating the relative hazards posed by various associated waste streams, including tank bottoms, oily debris, workover fluids, produced sand, and emulsions. It found that tank bottom samples exceeded the RCRA toxicity characteristics for benzene and lead. On the basis of these two EPA studies, the contaminants of concern for salt cavern disposal are arsenic, benzene, boron, cadmium, chromium, and lead.

Because these contaminants may behave differently in the environment than in the laboratory, an evaluation of the fate and transport mechanisms for each contaminant is presented in Section 4. On the basis of that evaluation, combined with a consideration of the hydrogeologic conditions in areas where cavern disposal is likely to occur (Section 5) and an assessment of potential release modes and exposure pathways (Section 6), a subset of the contaminants listed above that have the ability to produce human health risks was identified. Because risk is a function not only of the probability of exposure, but also of the potential for harm due to the chemical, the toxicity of these contaminants must also be assessed. Section 7 addresses the toxicity of this subset of contaminants, and in Section 8, the risks associated with exposure to releases of those contaminants considered dangerous to humans are estimated.

4. Fate and Transport for Contaminants of Potential Concern

In this section, the fate and transport of the contaminants of potential concern for salt cavern disposal is described. Specific information is provided for benzene, lead, arsenic, cadmium, chromium, and boron. This information is used in estimating contaminant concentrations at the location of a receptor for risk assessment.

4.1 Benzene

Benzene (C_6H_6) is the most important aromatic hydrocarbon in this study because of its physical properties. Benzene is unsaturated and reacts to add hydrogen and other elements to its ring of six carbon atoms.

Benzene, also known as annulene, carbon oil, and coal naphtha, is a clear, colorless to light yellow, watery liquid with an aromatic or gasoline-like odor. Benzene has a density less than that of water (0.8765 g/cm^3) (Mackay et al. 1992).

Benzene is a Class A carcinogen that has an EPA maximum contaminant level (MCL) of 0.005 mg/L (EPA 1994a). It is soluble in water (1.780 g/L at 20°C for fresh water) and readily volatilizes (changes from the aqueous to the gas phase) with a dimensionless Henry's Law constant of 0.2199 (Montgomery 1991; Montgomery and Welkom 1991). The Henry's Law constant gives the ratio of a compound's saturated vapor concentration to its concentration in the associated liquid phase and is an index of partitioning between dissolved and gaseous phases (Hern and Melancon 1987). For benzene, the effective half-life for volatilization is about 4.8 hours (Montgomery 1991; Montgomery and Welkom 1991). In saline water, the solubility of benzene decreases (Stumm and Morgan 1981).

In water, benzene has a distribution coefficient (mass of solute sorbed on solid surfaces per solid mass divided by the mass of solute per volume of solute [Freeze and Cherry 1979]), K_d , of 0.62 mL/g (Lyman et al. 1992). Sorption of benzene onto a solid surface produces a retardation of benzene's transport velocity in groundwater; that is, the velocity of the center of mass of a contaminant plume of benzene, V_c , will move at a retarded velocity of V/R , where V is the velocity of groundwater and R is a retardation coefficient. Retardation coefficients can be estimated by using the following relationship (Freeze and Cherry 1979):

$$R = 1 + \frac{\rho_b K_d}{\Phi} \quad (1)$$

where ρ_b is the bulk density of the matrix material, and Φ is its porosity (Freeze and Cherry 1979). For a bulk density of 1.7 g/cm^3 and a porosity of 0.1 (typical values for this study [Freeze and Cherry 1979]), the retardation coefficient for benzene is about 10.

Under aerobic conditions, benzene has an effective biodegradation half-life of about 10 days; for anaerobic conditions, its half-life is about 2 years (Howard et al. 1991). If exposed to air and sunlight, benzene undergoes photo-oxidation, with an effective half-life of 5-16 days; however, it does not apparently undergo hydrolysis (i.e., it does not react with water to form another compound [Mackay et al. 1992]).

As the above data show, benzene is very soluble in water, and once in a groundwater system, it is very mobile. Because of biodegradation and volatilization, however, it would have a somewhat limited range of travel in an aquifer. When biodegrading, benzene would be mineralized to form water (H_2O) and carbon dioxide (CO_2). Possible transformation products include cis-benzene glycol accompanied by partial dehydrogenation, yielding catechol, or cis,cis-muconic acid and α -hydroxymuconic semialdehyde (Montgomery and Welkom 1991). Because little information is available on the toxicity or fate and transport of these intermediate products, and their behavior can be site-specific, complete biodegradation of the decay products of benzene is assumed for this study.

4.2 Lead

Lead is generally found in the divalent form and tends to form relatively insoluble compounds with such common anions as hydroxide and sulfate. An insoluble precipitate can also form with sulfide, which can be present under reducing conditions. Lead can also form insoluble complexes with carbonate at pH values higher than 5.4 (Adriano 1986). In the presence of clays, lead is very immobile. An approximate K_d for lead is 900 mL/g (Baes and Sharp 1983; Baes et al. 1984). By using Equation 1 with a bulk density of 1.7 g/cm³ and a porosity of 0.1, the retardation coefficient for lead would exceed 15,000. The maximum recommended concentration of lead in drinking water is 0.015 mg/L (EPA 1994a).

Because of its low solubility, large distribution coefficient, and very large retardation coefficient, further analyses of lead-associated risks are not presented in this study.

4.3 Arsenic

Arsenic generally forms insoluble complexes, typically reacting with hydrous oxide coatings and various anions. For example, the solubility of pentavalent arsenic sulfide (As_2S_5) is 0.000136 g/L in cold, fresh water (CRC 1968). In brine, the solubility of arsenic would be less (Stumm and Morgan 1981). Arsenic readily adsorbs onto clays, iron or manganese compounds, or aluminum complexes. Arsenic can also be immobilized by forming complexes or chelates with iron or calcium (Callahan et al. 1979). The distribution coefficient for trivalent arsenic reported for agricultural soils and clay ranges from about 1- 8 mL/g; for pentavalent arsenic, the range is approximately 2 - 18 mL/g (Baes and Sharp 1983). For this study, a K_d of 10 mL/g was assumed. By using Equation 1 with a bulk density of 1.7 g/cm³ and a porosity of 0.1, the retardation coefficient for arsenic would be about 170 (rounded to 200). The MCL for arsenic is 0.05 mg/L (EPA 1994a).

Because of the low solubility and large distribution coefficient of arsenic, its concentration and mobility in groundwater would be very low.

4.4 Cadmium

Cadmium can exist as soluble or insoluble species or can be immobilized by sorption onto clays or iron oxides. Cadmium forms soluble complexes and insoluble precipitates with carbonates and hydroxide ions, and it can also exist as the hydrated ion (Baker and Amacher 1982). Under acidic conditions, cadmium can be relatively mobile, with its mobility decreasing as increasing pH and ion exchange capacity increase (Lu et al. 1975). In soil that contains clay and iron hydroxides, cadmium has a low mobility and commonly coprecipitates with iron and manganese hydroxides.

The solubility of cadmium is generally low; however, the solubility of cadmium chloride is about 140 g/L in cold, fresh water, and that of cadmium hydroxide is about 0.00026 g/L (CRC 1968). In brine, this solubility would be less (Stumm and Morgan 1981). The K_d values for cadmium in soil and clay range from about 1.3 to 27 mL/g (Baes and Sharp 1983). For this study, a K_d value of 3 mL/g was used. By using Equation 1 with a bulk density of 1.7 g/cm³ and a porosity of 0.1, the retardation coefficient for cadmium would be about 50. Cadmium has an MCL of 0.005 mg/L (EPA 1994a).

Because of the presence of iron in the tank bottom wastes, cadmium is likely to precipitate out as a hydroxide. Given the low solubility of cadmium hydroxide and its moderate rate of sorption, the mobility of cadmium in groundwater would be low.

4.5 Chromium

The predominant form of chromium likely to occur in the vicinity of a failed salt cavern would be insoluble, trivalent chromate (Cr₂O₃) (ATSDR 1989). Soluble chromate generally forms precipitates, with hexavalent chromium undergoing anion adsorption and reduction, and trivalent chromium undergoing adsorption, hydrolysis, and chelation (Reisenauer 1982). Manganese and iron oxides can affect chromium adsorption. Adsorption of all chromium species can occur in substrates in the pH range of 6 to 7.5, making the chromium fairly immobile. Adsorption of the hexavalent form can decrease with increasing pH, while adsorption of the more predominant trivalent form can increase with increasing pH, probably as a result of cation exchange (Adriano 1986). In the presence of organic matter, hexavalent chromium is converted to the more insoluble trivalent form. The hydrated form of trivalent chromium sulfate [Cr₂(SO₄)₃] has a solubility of about 120 g/L in cold, fresh water (CRC 1968). Brine conditions would be expected to reduce this solubility. The K_d values reported for soil and clay range from about 1.2 - 1,800 mL/g for the hexavalent form and 470 - 150,000 mL/g for the trivalent form (Baes and Sharp 1983). A K_d value of 30 mL/g was assumed for this study. By using Equation 1 with a bulk density of 1.7 g/cm³ and a porosity of 0.1, the retardation coefficient for chromium would be about 500. Total chromium has an MCL of 0.1 mg/L (EPA 1994a).

Because of low solubility and high distribution coefficients, both trivalent and hexavalent forms of chromium are expected to have low concentrations and mobilities in groundwater. The mobility of the hexavalent form, however, is expected to be greater than that of the trivalent form.

4.6 Boron

Boron is a nonvolatile metalloid that occurs in combination with most of the other elements. Boron readily hydrolyzes in water to form the electrically neutral, weak monobasic acid H_3BO_3 and the monovalent ion $\text{B}(\text{OH})_4^-$ (ATSDR 1990). Although most boron compounds are highly soluble in water (Rai et al. 1986), boron may be precipitated with aluminum, silicon, or iron in the form of fairly insoluble hydroxyborate compounds on the surfaces of minerals. In elemental form, boron is insoluble in water (Windholz et al. 1983). The adsorption of boron may not be reversible in some media. This irreversibility may be the result of solid-phase formation on mineral surfaces. Little information is available on boron sorption; however, for clays, K_d may be as high as 20 mL/g, with a range for soils of 0 to 10 mL/g (Sheppard et al. 1984). For this study, a K_d value of 8 mL/g was assumed. By using Equation 1 and values for bulk density of 1.7 g/cm^3 and for porosity of 0.1, the retardation coefficient for boron would be about 150. As of 1994, the EPA did not have any defined drinking water standards for boron, although its lifetime health advisory is 0.6 mg/L for a 70-kg adult (EPA 1994a).

It is likely that boron would precipitate to form insoluble hydroxyborate compounds on mineral surfaces because of the iron and silicon content of the tank bottoms component of the wastes. Because of this precipitation, further analyses of boron-associated risks are not presented in this study.

5. Hydrogeology

As discussed in Section 2, the majority of salt formations of interest for waste disposal occur along the Gulf Coast and in Texas and New Mexico, although other states, such as Kansas and Michigan, could also be considered as potential candidate states for NOW disposal in salt caverns. The following sections discuss hydrogeological conditions for the Gulf Coast, the western Texas panhandle, and New Mexico. A composite of these areas is then used for a generic analysis of disposing of NOW in a hypothetical salt cavern in domal salt. Additional site-specific calculations are recommended for future studies in other states and bedded salt formations.

5.1 Gulf Coast Hydrogeology

Salt caverns along the Gulf Coast of the United States are located in the Coastal Plain Physiographic Province (Back et al. 1988). This province is underlain by a gulfward thickening wedge of unconsolidated to semiconsolidated sedimentary rocks (sand, silt, and clay derived from erosion of nearby continental upland areas). These sediments overlie consolidated rocks of Mesozoic Age and range in thickness from a few feet near their landward limit to more than 30,000 ft in southern Louisiana.

As part of the Gulf Coast Regional Aquifer-System Analysis (GCC RASA) program, the depth to groundwater was evaluated for a 230,000-mi² study area that included coastal regions in Texas, Louisiana, Mississippi, and Florida (Williams and Williamson 1989). Based on data from 6,825 wells, the depth to the water table ranges from 0 to 74 ft, with a median value of 20 ft. This shallow groundwater system is primarily composed of sands interbedded with deposits of silt and clay. Where the silts and clay have been eroded and the aquifer is in communication with the atmosphere, the aquifer is unconfined. Confined to semiconfined conditions exist where low-permeability clays and silt overlay the more permeable sands (Hanor 1993). Beneath the shallow groundwater system are other sequences of clays and silts, interspersed with beds of sand. The sand areas constitute other potential aquifers that are predominantly confined (Capuano and Jan 1996).

Recharge to the shallow groundwater system is derived from precipitation. The majority of recharge occurs in areas where the clay and silt layers are absent. Discharge of this aquifer occurs to surface waters, underlying deeper aquifers, and pumping wells.

5.2 Texas and New Mexico Hydrogeology

Bedded salt occurs in the Texas panhandle area and West Texas, as well as in central and southeastern New Mexico. These bedded salts are located, for the most part, in deep formations (the top of salt occurs at a depth of 500 to 2,000 ft below the land surface, and the salt thickness is about 1,000 to 3,000 ft thick). Although most of these bedded salts occur below 1,000 ft, some of the bedded salts in west Texas can be much shallower (e.g., one of the Permian Brine Sales' caverns starts at a depth of about 700 ft [Hickerson 1995]).

Overlying the bedded salt layers are the Ogallala fluvial aquifer, which is composed of stream and river deposits, and the Dockum aquifer, which is composed of fluvial and lacustrine (lake) deposits (Bassett and Bentley 1982). These aquifers make up a shallow, fresh-water system that is used for domestic, municipal, industrial, and agricultural purposes. The combined thickness of these two aquifers can be as great as 2,300 ft (Bair et al. 1985). The Ogallala is the shallower of the two aquifers and occurs at a depth that ranges between 20 and 400 ft (Wood and Sanford 1995). It has a thickness that ranges from 0 to 800 ft (Seni 1980), and it underlies about 134,000 mi² of land that extends from Nebraska to New Mexico (Back et al. 1988). Its principal composition is sand and gravel.

The Dockum aquifer lies below the Ogallala aquifer. Locally, its depth is variable; it can outcrop at the surface or occur as deep as 800 ft below the ground. It is typically composed of a sandstone and conglomerate unit (fluvial) overlying a fine silt and clay unit (lacustrine). The thick Permian evaporite-bearing unit beneath the Dockum is an aquitard and a barrier to vertical groundwater flow. Depth to bedded salt ranges from about 500 to 2,000 ft. The uppermost extensive salt is the Salado Formation. Where this unit has been dissolved, various older formations (e.g., Seven Rivers, Grayburg, San Andres, and Castile) contain the uppermost salt units. In some areas, salt has been completely removed.

Bedded salts are being developed for low-level nuclear waste disposal at the Waste Isolation Pilot Plant (WIPP) in New Mexico. The facility has been constructed and will shortly begin operation. It is located at a depth of 2,150 ft below the ground surface in the Salado Formation (DOE 1990). The Ogallala and Dockum aquifers are absent in this area of New Mexico, and the shallowest groundwater of consequence occurs in the Culebra Dolomite of the Rustler Formation at a depth of about 750 ft.

Recharge to the shallow groundwater system in the semi-arid Texas/New Mexico environment is derived from precipitation. Wood and Sanford (1995) estimate the annual recharge to be 11±2 mm/yr. Recharge is small because of high potential evaporation, plant transpiration, limited precipitation, and runoff. In the past, discharge was to springs; other, deeper, groundwater systems; and pumps. Because of heavy pumping, most of the discharge springs are now dry, and the only discharge is to deeper aquifers.

In general, water quality in Texas and New Mexico decreases with depth. For example, the Rustler Formation water quality is generally poor, with total dissolved solids ranging from 286 mg/L in Ward County to 157,000 mg/L in Winkler County. Chloride concentrations can be as high as 89,700 mg/L in Winkler County, Texas (Richey et al. 1985). Because of this poor water quality, water for public water supply, irrigation, industry, livestock, and rural domestic use is often obtained from overlying aquifers, such as the Santa Rosa Sandstone Formation in the Dockum and from the Cenozoic alluvium in the Delaware basin (including the Ogallala Aquifer, if present). In the Texas panhandle area, similar observations have been made on groundwater quality (Bair 1987); i.e., total dissolved solids and the concentration of brine increase with depth.

6. Release Calculations

Impact analyses were performed for the general categories of cavern-release scenarios discussed in Section 2: inadvertent intrusion; failure of the cavern seal; release of contaminated fluid through cracks, leaky interbeds, or nonhomogeneous zones of higher impermeability; and partial cavern roof fall. Details on these analyses are presented in Section 6.2. Concentrations for the contaminants of potential concern presented in these sections are used for risk analyses in Section 8.

For all of the release scenarios, the initial concentrations of contaminants leaving the cavern must be known. These concentrations are discussed in Section 6.1.

6.1 Initial Concentrations for Contaminants Released from a Cavern

In the event of a release, some of the brine overlying the waste would leave the cavern. This brine will contain dissolved contaminants of potential concern. No data are available to show the chemical characteristics of the cavern brine at the time of release, because no disposal cavern has yet been closed. After the cavern is closed, the chemical constituents of the waste will reach an equilibrium solubility with the overlying brine. Theoretical solubility values for the four constituents of potential concern (benzene, arsenic, cadmium, and chromium) are available in the literature (e.g., ATSDR 1989; CRC 1968; Montgomery 1991; and Montgomery and Welkom 1991), but these values are based on the solubility of the contaminants in cool, fresh water using pure laboratory-grade chemicals and are not relevant for in-cavern conditions.

The conditions found in a closed cavern will have a significant effect on final solubility. Two factors that are especially important are the salt content and the pH of the water in the cavern. Fresh water will dissolve more organic materials (e.g., benzene) than brine. Consequently, the brine will reach an equilibrium benzene concentration with the waste that is lower than the theoretical fresh water solubility. In addition, the brine in the cavern will contain chloride, sulfate, sodium, calcium, and hydroxide. Many toxic metals form insoluble precipitates with one or more of these ions, which will limit the solubility of the metals. Also some ions of arsenic form insoluble calcium compounds.

One of the main types of waste disposed of in salt caverns is drilling waste, which tends to be alkaline. The presence of a high-pH waste will cause the cavern brine to have a pH higher than neutral. The solubility of metals is much higher at low pH values than at the higher pH values expected in the cavern brine. Therefore, the brine will reach equilibrium metals concentrations with the waste that are somewhat lower than the theoretical fresh-water solubilities.

One way of estimating the chemical characteristics of the cavern brine is to look at other brines that have been in contact with both crude oil and many of the solid materials that will be in the wastes for a long enough time to reach equilibrium values. Perhaps the best example of such brines is produced water. Produced water characteristics vary somewhat, but extensive data are available to estimate chemical concentrations. The following analyses contain data on

concentrations of chemical constituents in produced water:

- As part of its proposed effluent limitations guidelines for the coastal oil and gas industry, EPA sampled ten coastal oil and gas facilities for produced water constituents (SAIC 1994).
- EPA summarized several produced water studies covering 55 facilities as part of its final effluent limitations guidelines for the offshore oil and gas industry (EPA 1993).
- EPA (1987) selected median and upper 90th percentile concentrations for arsenic and benzene in produced water as inputs to a risk assessment model.

Concentration ranges for the constituents of concern cited in these three studies are given in Table 6-1.

Another approach for estimating fully saturated brine concentrations is to look at the relative proportions and concentrations of the major waste types that are placed into the caverns and to estimate how much of those wastes will leach into the cavern brine. The operators of the four disposal caverns in Texas were asked to provide qualitative estimates of the proportions of different types of wastes entering the caverns. Depending on the operator, drilling wastes make up from 20-50% and tank bottoms make up about 50-60% of the total incoming waste stream¹. Miscellaneous wastes make up the remainder. In many cases, the solids in the wastes contain chemical concentrations much higher than those reported for produced water. However, under conditions where wastes are in contact with water, concentrations of chemicals in the surrounding water are typically much lower than those in the waste. The amounts of chemicals likely to leach out of the waste when it is exposed to water have been estimated by EPA.

The EPA (1987) provides comparative data on both drilling waste solids and solids that have undergone the toxicity characteristic leaching procedure or TCLP (40 CFR 261, Appendix II). The TCLP test measures a waste's tendency to leach into water. The TCLP can serve as an analog of the extent to which wastes in a cavern will leach into the overlying brine. In the TCLP, solids samples are extracted by mixing them for 18 hours in a flask containing water adjusted to an acidic pH. Because metals are more likely to leach out of a solid under low pH conditions, the TCLP test is more conservative than leaching at a neutral pH. Under these conservative, low-pH conditions, the upper 90th percentile TCLP results are much lower than the results from analysis of drilling waste solids, which had been measured without being subjected to leaching (see Table 6-1). These data support the premise that only a small fraction of the total waste is likely to leach into water or the cavern brine.

The other major type of waste disposed of in caverns is tank bottoms. The EPA (1994b)

¹Telephone conversations between John Veil, Argonne National Laboratory, Washington, DC, and Russ Hickerson, Permian Brine Sales, Odessa, TX; Grady Moore, Taylor Disposal Operating, Inc., Carthage, TX; and Tom Voskamp, Voskamp Exploration, Midland, TX, on March 12, 1997.

provides extensive characterization of tank bottoms. The range of TCLP values and analysis of samples as reported in EPA (1994b) for tank bottoms at production facilities (the predominant source of tank bottoms likely to go to the caverns) are shown in Table 6-1. Only a small fraction of the total tank bottom chemical concentration is likely to leach into water or the cavern brine.

For the initial concentrations of constituents to be used in the fate and transport modeling in this report, we have chosen the highest concentration for each constituent of concern from the (a) produced water data, (b) drilling waste TCLP data, and (c) tank bottoms TCLP data. In each of these data sets, we already are looking at the maximum concentrations, which typically are many times higher than average values. The concentrations of the contaminants of potential concern in brine when they leave the cavern under different release modes are as follows: benzene, 20.4 mg/L; arsenic, 1.7 mg/L; cadmium, 0.29 mg/L; and chromium, 0.85 mg/L.

6.2 Cavern Release Scenarios

Five release scenarios are discussed in this section: inadvertent intrusion, which could produce a release of cavern fluid to the ground surface; failure of the cavern seal, which could release contaminated fluid to the groundwater (the release could be either at the depth of the cavern or at more shallow depths); release of contaminated fluid through cavern cracks; release of contaminated fluid through leaky interbeds or non-homogeneous zones of higher permeability material; and a partial cavern roof fall, which could release contaminated fluid to deep or shallow groundwater depending on the condition of the cavern seal. Calculations for these release scenarios are discussed below.

6.2.1 Inadvertent Intrusion

In the inadvertent intrusion scenario, an exploratory well for oil or minerals penetrates a hypothetical waste disposal cavern that has an initial brine volume of one million ft³ (about 7.5 million gallons). Assuming that the cavern contains 750,000 ft³ of NOW when full, approximately 2 million gallons of brine lie above the NOW. Groundwater wells probably would not reach the cavern because drinking or irrigation water could be obtained at shallower depths, and groundwater at the depth of the cavern would probably not be potable because of brine (Section 5). Based on an average modulus of elasticity of 337,000 psi (Streeter 1961), a depth of 1,500 ft, and an initial pressure in the cavern equal to the lithostatic pressure (about 1,500 psi for a depth of 1,500 ft assuming a lithostatic pressure gradient of 1 psi per ft [SMRI 1997]), a maximum of about 2,000 gallons of contaminated fluid would flow from the cavern toward the surface. This value is about 0.1% of the fluid present in the cavern. In addition to brine and dissolved waste constituents, drilling muds and other associated fluids would also flow toward the surface.

If the blowout-protection system of the well failed, fluids from the cavern could spill onto the ground surface and form a pool in the vicinity of the well pad or be discharged into a lined pond. If the discharge occurs directly to the ground and the local topography is depressed, a small surface pond would form. If the pond has a radius of 25 ft, the depth of the spill would be

provides extensive characterization of tank bottoms. The range of TCLP values and analysis of samples as reported in EPA (1994b) for tank bottoms at production facilities (the predominant source of tank bottoms likely to go to the caverns) are shown in Table 6-1. Only a small fraction of the total tank bottom chemical concentration is likely to leach into water or the cavern brine.

For the initial concentrations of constituents to be used in the fate and transport modeling in this report, we have chosen the highest concentration for each constituent of concern from the (a) produced water data, (b) drilling waste TCLP data, and (c) tank bottoms TCLP data. In each of these data sets, we already are looking at the maximum concentrations, which typically are many times higher than average values. The concentrations of the contaminants of potential concern in brine when they leave the cavern under different release modes are as follows: benzene, 20.4 mg/L; arsenic, 1.7 mg/L; cadmium, 0.29 mg/L; and chromium, 0.85 mg/L.

6.2 Cavern Release Scenarios

Five release scenarios are discussed in this section: inadvertent intrusion, which could produce a release of cavern fluid to the ground surface; failure of the cavern seal, which could release contaminated fluid to the groundwater (the release could be either at the depth of the cavern or at more shallow depths); release of contaminated fluid through cavern cracks; release of contaminated fluid through leaky interbeds or non-homogeneous zones of higher permeability material; and a partial cavern roof fall, which could release contaminated fluid to deep or shallow groundwater depending on the condition of the cavern seal. Calculations for these release scenarios are discussed below.

6.2.1 Inadvertent Intrusion

In the inadvertent intrusion scenario, an exploratory well for oil or minerals penetrates a hypothetical waste disposal cavern that has an initial brine volume of one million ft³ (about 7.5 million gallons). Assuming that the cavern contains 750,000 ft³ of NOW when full, approximately 2 million gallons of brine lie above the NOW. Groundwater wells probably would not reach the cavern because drinking or irrigation water could be obtained at shallower depths, and groundwater at the depth of the cavern would probably not be potable because of brine (Section 5). Based on an average modulus of elasticity of 337,000 psi (Streeter 1961), a depth of 1,500 ft, and an initial pressure in the cavern equal to the lithostatic pressure (about 1,500 psi for a depth of 1,500 ft assuming a lithostatic pressure gradient of 1 psi per ft [SMRI 1997]), a maximum of about 2,000 gallons of contaminated fluid would flow from the cavern toward the surface. This value is about 0.1% of the fluid present in the cavern. In addition to brine and dissolved waste constituents, drilling muds and other associated fluids would also flow toward the surface.

If the blowout-protection system of the well failed, fluids from the cavern could spill onto the ground surface and form a pool in the vicinity of the well pad or be discharged into a lined pond. If the discharge occurs directly to the ground and the local topography is depressed, a small surface pond would form. If the pond has a radius of 25 ft, the depth of the spill would be

about 1 inch without considering evaporative losses. For a spill this small, fluids from the cavern would not reach the underlying unconfined aquifer that occurs at a median depth of 20 ft (Section 5.1), but would form a contaminated zone in the unsaturated soil. If the porosity of the soil is 0.3 (Freeze and Cherry 1979), a mass-conservation calculation shows that the penetration depth of the fluids from the cavern would be less than 6 inches. Mobilization of contaminants out of the contaminated zone could then occur by leaching. However, remediation activities at the site (e.g., removal of contaminated soil) would occur before the contaminants could dissolve and be transported by advection and dispersion to the water table.

In addition to lasting for a short duration, the pond water would be very unappetizing for ingestion (i.e., the water would have a very high turbidity because of the drilling mud, it would be very salty [saturated brine], it would be oily because of the presence of organic materials, and it would probably have an unpleasant odor). Because the volume of released fluid for this scenario would be small, the effects would be of very short duration, the liquid would not be potable, and such a spill would be quickly remediated, the scenario was eliminated from further analyses.

6.2.2 Release through the Cavern Seal

For this scenario, the seal that keeps liquids within the cavern is assumed to fail and release brine and contaminants to the well bore. As discussed in Section 2.4, the well bore would have cement plugs installed during cavern closure and abandonment. With time, the well casing may deteriorate because of the presence of brine in the vicinity of the caprock or the top of the cavern if a caprock is not present. For anticipated conditions, the well casing will corrode and fail near the top of the cavern first. With additional time, the well casing will fail at shallower depths.

Once the cavern is full of waste, it would be sealed and abandoned. At the time of sealing, the cavern would be mostly filled with solids and semisolids that are not fully compacted. Brine would remain between the top of the cavern and the top of the waste mass.

As discussed in Section 2.4, the pressure in the cavern would increase because of the combined effects of the addition of sensible heat from the surrounding salt and salt creep. Although the pressurization of sealed caverns containing liquids or dry granular wastes is currently under investigation (e.g., Langer et al. 1984; Wallner 1986; Berest and Brouard 1995; Wallner and Paar 1997; and Berest et al. 1997a), little research has been directed at predicting pressure behavior in caverns containing NOW. Future work should be performed to reduce the uncertainty in this process.

For this scenario, the pressure in the cavern is assumed to reach a high enough value that the cavern seal fails because of a crack in the plug, dissolution of salt around the seal, or by some other means. Contaminated fluid then moves up the well bore toward the ground as the pressure in the cavern is reduced to the hydrostatic value.

Assuming that the cavern had an initial brine volume of 1,000,000 ft³, and that it was filled to three-quarters of its capacity with NOW, about 250,000 ft³ of free brine and 750,000 ft³ of

waste would be present. If the cavern failed at a pressure equal to the lithostatic value (approximately 1,500 psi for a cavern located at a depth of 1,500 ft), a maximum of only about 0.1% of the free liquid (about 2,000 gal) would exit the cavern because of the effects of compressibility (Streeter 1961), if the well bore was free of liquid and at atmospheric pressure. If the well bore contained water, or if the released volume was greater than the volume of the well bore up to the location of the deepest bridge plug, less than 0.1% of the fluid would escape from the cavern. For conservative results, this study assumes that the full 0.1% volume would be released.

Flow of the released fluid would be greatly restricted in the well bore at the locations of the cement bridge plugs. Flow through the bridge plugs would resemble flow through a porous medium having a low hydraulic conductivity (about 1×10^{-8} to 1×10^{-5} cm/s), similar to that of cemented sandstone (Maidment 1993). If the cavern fluid moves up the borehole at a rate equal to the saturated hydraulic conductivity of the cement (Freeze and Cherry 1979), it would have a velocity between 3×10^{-5} and 0.03 ft/d. For a cavern at a depth of 1,500 ft, fluid would not reach the surface for about 140 years if the well casing remained intact, and evapotranspiration did not deplete the volume of free liquid near the ground surface.

While moving up the borehole, fluid from the cavern could also move laterally into adjoining formations if the well casing had failed. Because the casing would probably be made of ordinary steel, there is a high probability that the casing would fail when exposed to groundwater containing brine over a time period ranging into the thousands of years. Two possible cases are considered under this scenario: (1) the casing fails at the depth of the cavern (at or near the cavern roof) and contaminated fluid is released to a deep aquifer, and (2) the casing fails at a shallow depth and releases fluid to a near-surface aquifer. Because of hydrogeological differences between the aquifers considered, these scenarios are discussed separately below.

For a deep casing failure, fluid moving up the well bore would move into the deep aquifer and be transported laterally. The presence of low-permeability beds at shallower depths would prevent vertical transport of the contaminated fluid to overlying aquifers and the ground surface. Assuming that the well bore has a diameter of 2 ft and that the ambient groundwater velocity is 10 ft/year, contaminated water would enter the surrounding porous medium for a period of about 0.2 years.

The extent and magnitude of contamination created by this type of release would depend on the hydrological properties of the material in the vicinity of the failed casing, the volume of fluid that is released, the duration of the discharge, and the transport properties of the contaminants. In the vicinity of the cavern, hydrological properties are unlikely to favor rapid transport of the contaminants. For example, the groundwater velocity at depth is estimated on the basis of engineering judgment to be less than 10 ft/yr. Because of adsorption and subsequent retardation (Section 4.1), contaminants (particularly metals) would be transported at even lower velocities. For example, cadmium, which has a distribution coefficient of 3 mL/g (Section 4.4), would have a retardation coefficient, R , of about 50 for an assumed bulk density of 1.7 g/cm^3 and

a porosity of 0.10 (Equation 1). Therefore, the center of mass velocity of cadmium would be 50 times less than that of the groundwater (0.2 ft/yr). In 100 years, cadmium would travel about 20 ft.

Benzene would move much more quickly than the dissolved metals because of its greater mobility. As discussed in Section 4.1, benzene has a distribution coefficient of about 0.6 mL/g and a retardation coefficient of about 10. In 100 years benzene would, therefore, move about 100 ft. Unlike the metals, however, benzene would be likely to degrade biologically with time. For the calculations presented in this study, benzene was assumed to have an effective half-life of 2 years, the upper end of the values for anaerobic conditions presented in Section 4.1. In 100 years, its concentration would decrease by a factor of about 1.0×10^{15} (50 half-lives).

In addition to the extent of contamination created by the release, the contaminant's concentration is also needed for risk assessment. In general, the downstream concentrations of contaminants depend on the length of time that the cavern acts as source of contaminated fluid. For either a release at the depth of the cavern or to a shallow aquifer, the cavern is assumed to depressurize to conditions in the well bore within one day. Fluid released during the depressurization would then be swept into adjacent aquifers by moving groundwater (10 ft/yr at the depth of the cavern and 100 ft/yr for a shallow release). Under these conditions, a two-foot well bore would act as a source of contamination for 0.2 and 0.02 years at the depth of the cavern and in a shallow aquifer, respectively. After the system depressurizes, salt creep would once again occur and the pressure in the cavern would increase, particularly if the point of failure self-heals. Because of this repressurization, the seal may again fail, and the process can then repeat itself as a series of short, pulsed releases. Because the time between releases would be long (repressurization is a slow process), the pulses would not interact with each other along the flow path.

Contaminant concentrations in the exiting fluid are discussed in Section 6.1 and are listed in Table 6-1. Because of the short duration time of a pulse release scenario, little dilution would occur because of mixing with uncontaminated groundwater. The contaminant concentrations in the water adjacent to the failure point would, therefore, be the same as in the cavern.

After release, the aqueous phase contaminants would be transported in the direction of lower hydraulic head (pressure) and would undergo sorption (loss of material to particle surfaces), dispersion (reduction in concentration produced by non-uniform fluid velocities), and degradation (decrease in concentration produced by chemical or biological interactions). Transport calculations were performed with a one-dimensional analytical solution to the governing partial differential equation incorporating advection, dispersion, and biodegradation (Tomasko 1991; 1994) to estimate the concentrations of benzene, cadmium, arsenic, and chromium at a lateral distance of 1,000 ft from the location of the casing failure, the assumed location of the nearest human receptor.

For transport calculations, the groundwater velocity was assumed to be 10 ft/yr and dispersion was assumed to be scale dependent, with dispersivity set equal to one-tenth of the

travel distance (Lallemand-Barres and Peaudecerf 1978). Contaminant concentrations in the groundwater were evaluated at the location of a potential receptor at a time of 1,000 years in the future, a typical value for risk analyses. In the case of cadmium released to shallow aquifers, the maximum estimated concentration would reach the receptor after 334 years. This value is noted, where applicable, in the tables associated with Section 8 and is used in the risk calculations. A compilation of contaminant concentrations for these conditions is given in Table 6.2. As shown in Table 6.2, the concentration of benzene would be 0.0 mg/L at 1,000 years because of degradation along the flow path (approximately 500 half-lives). Values for arsenic and chromium would both be very small because of retardation along the flow path and the short duration of the release (0.2 yr).

For the second alternative considered for this release scenario, the cavern seal is again assumed to fail; however, the well bore casing at depth is assumed to be intact. Contaminated fluid then flows up the well bore and exits the casing at a failure point adjacent to a shallow groundwater aquifer such as the Dockum or the Ogallala. The initial concentration of the contaminants entering the system would be the same as for the scenarios discussed above (Table 6-1), and there would be no substantial dilution. The duration of the source term would be ten times less than that used at depth because of the higher groundwater velocity in the shallow groundwater system (100 ft/yr). For a release to shallow groundwater, the concentrations (Table 6.2) would be larger than those discussed above because of shorter travel time. The concentration of benzene, however, is still at 0.0 mg/L because of its biological degradation. In spite of the higher velocity and shorter travel time for a shallow groundwater release, the contaminant concentrations at the receptor 1,000 years after the release would all be much less than their MCLs discussed in Section 4 (Table 6.2).

6.2.3 Release of Contaminated Fluid through Cracks

During pressurization of the cavern because of the combined effects of thermal heating and salt creep, cracks might develop that would release fluid into the surrounding material, thereby reducing the pressure in the cavern. The volume of fluid released would be a function of the pressure in the cavern, the volume of the cracks, and the crack pressure. If the pressure in the cracks is atmospheric, the volume of fluid released would be the same as that discussed under the inadvertent intrusion scenario (2,000 gallons). However, the actual volume released could be much less than this value if the cracks are at the local hydrostatic or lithostatic pressure. For conservative results, the volume of released fluid is assumed to be 2,000 gallons.

Depending on the pressure in the cracks, they could self-heal after the release because of additional salt creep. With repressurization of the cavern, the cracks could once again open, producing a series of short contaminant pulses (probably on the order of hours to days in duration) that would not interact with one another because of the time needed to repressurize the cavern to a value that approaches or exceeds the local lithostatic value. Because of gradients in the lithostatic pressure, cracks would open in a vertically upward direction (SMRI 1997). With time, the contaminated fluid in the cracks could reach a deep underground aquifer and be

transported laterally to the location of a potential receptor (1,000 ft away from the point of release).

The contaminant concentrations at the location of the receptor 1,000 years after the release into the underground aquifer would be the same as those presented above for failure of the cavern seal with a subsequent pulsed release at the depth of the cavern (Table 6.2). The resulting contaminant concentrations would all be much less than their associated MCLs (Section 4).

6.2.4 Release of Contaminated Fluid through Leaky Interbeds or Nonhomogeneous Zones

In this scenario, the cavern is assumed to have a leaky interbed or heterogeneity that allows communication with the outside environment. As the cavern pressure rises because of thermal effects and salt creep, fluid would be discharged into the interbed where it would be laterally transported under existing gradients. Fluid velocity in the interbed is assumed to be 10 ft/yr. In this way, the entire fluid volume of the cavern would eventually be discharged into the surrounding material.

Van Sambeek (1993) gives the following formula for the steady-state volumetric creep rate for a cylindrical cavern:

$$\frac{dV}{dt} = -\sqrt{3} \left(\frac{\sqrt{3}}{n} (P_{\infty} - P_i) \right)^n A \exp \left(-\frac{Q}{RT} \right) \quad (2)$$

where

- n, A, and Q/R = Model calibration parameters,
- P = Lithostatic pressure,
- P_i = Internal pressure of the cavern,
- t = Time, and
- T = Temperature in degrees Kelvin.

Parameters for the above equation are compiled in Berest et al. (1997b). For this analysis, the following values were selected as typical: n = 5, T=304K, Q/R=7,500, and A=100,000. For a brine-filled cavern,

$$P_{\infty} - P_i = 0.1 H \quad (3)$$

where H is the depth of the cavern (Berest et al. 1997b).

Using a value of 533 m for H (top of cavern at a depth of 1,500 ft plus 250 ft of free brine), and the above parameters, the steady-state volumetric creep rate from Equation 2 expressed as a percent would be about -0.007% per year. At this rate, it would take about

14,000 yr to discharge the cavern fluid to the interbed. For 2 million gallons of free brine in the cavern, the steady-state leak rate would, therefore, be about 150 gal/yr.

The leaking brine would mix with in-situ water and be transported down-gradient. Because of this mixing, the contaminant concentrations would be reduced by dilution. Dilution, D_f , can be expressed by the following expression (Tomasko 1991):

$$D_f = \frac{Q_g}{Q_{av}} + 1 \quad (4)$$

where Q_{cav} is the volumetric leak rate of the cavern and Q_{gw} is the volumetric flow in the interbed. For a cavern that has a diameter of 100 ft, an interbed thickness of 20 ft, and a groundwater velocity of 10 ft/yr, the dilution factor would be 1,000.

Table 6-2 lists the contaminant concentrations at the receptor for this scenario at a time of 1,000 years after the cavern has begun to leak. All of the concentrations are small compared to their MCLs.

6.2.5 Partial Cavern Roof Fall

Loss of cavern integrity through a partial roof fall coupled with failure of the cavern seal could produce impacts similar to those described in Section 6.2.2. Under these scenarios, the cavern would discharge fluid in a series of short pulses separated by periods of low to no discharge when the pressure in the cavern is increasing because of salt creep. If a partial roof fall occurs without failure of the cavern seal, the release of contaminated fluid would occur as a series of short pulses. A partial roof fall coupled with a release through leaky interbeds or non-homogeneous zones of higher permeability material would be manifested as a long slow release. Contaminant concentrations for these various scenarios are given in Table 6-2.

6.2.6 Probabilities of Occurrence

In performing a risk assessment, besides the concentrations of the contaminants of concern being required, the probability that a given scenario would occur also needs to be known. Because there is no operational history for disposing of NOW in salt caverns, the probabilities of occurrence for the release scenarios described above are uncertain. Under the most optimistic conditions, no releases would ever occur, and the associated probabilities of occurrence would be 0.0. For the most pessimistic conditions, releases would always occur and the probabilities of occurrence would be 1.0.

In order to reduce the uncertainty in the range of the probabilities of occurrence, a questionnaire was distributed to experts in the field of salt disposal. The panel of experts was asked to provide both a "best-estimate" and a "worst-case" estimate of the probability of occurrence for each of the release scenarios. In the context of this questionnaire and study, best

estimate did not refer to the "best-case" or the best or least risky case, but rather it referred to the probability of occurrence that was most likely in the best judgment of the expert. Similarly, "worst-case" referred to the least likely probability of occurrence in the best judgment of the expert rather than to the most risky case.

Following the receipt of responses from the expert panel, the estimates were aggregated to form consensus values for each of the probabilities of occurrence. A number of procedures can be used to form the consensus values from the individual estimates. These include behavioral and mechanical approaches (Winkler and Sarin 1981). In behavioral aggregation, some contact is required between the experts. The range in estimates provided is then reduced through intensive group interaction. This methodology is typically followed in the Delphi approach of Brown and Helmer (Brown and Helmer 1964). With mechanical aggregation, a mechanical rule is used to combine the estimates of the probabilities. For example, the aggregate value can be the arithmetic mean, median, weighted average, or some other weighting that uses Bayesian estimation by incorporating *a priori* information (Winkler 1968; Winkler 1977; Makridakis and Winkler 1983). For the present study, an arithmetic average was used to represent the aggregate value for the probabilities of occurrence. This method was selected because of the difficulties and time constraints of using a Delphi approach, the lack of appropriate weighting functions for the experts (there is no cavern release data available that could be used to rank the ability of the experts according to past predictions [Winkler and Clemen 1992]), and the average value of the data performs as well as any of the other mechanical rules (Winkler 1968).

Table 6-3 lists the best-estimate and worst-case aggregated probabilities of occurrence for the release scenarios previously discussed and their ranges. For all cases, the highest probabilities of occurrence were for a partial fall of the roof (0.10 and 0.29, respectively). The smallest probabilities of occurrence were for a partial roof fall with a cavern seal failure and release to a shallow aquifer (0.006 and 0.051, respectively), and a cavern seal failure with subsequent release to a shallow aquifer (0.012 and 0.040, respectively).

7. Toxicity of Contaminants of Potential Concern

Toxicity assessment is a key component in risk assessment. It weighs available evidence regarding the potential for the contaminants of concern to cause adverse effects in exposed individuals. It consists of two parts: hazard identification and dose-response evaluation. The hazard identification process determines whether exposure to a contaminant can cause an increase in the incidence of a particular adverse health effect (e.g., cancer, birth defect) and whether that effect is likely to occur in humans. Section 7.1 describes the potential health hazards associated with the contaminants discussed in Section 4, that is, those contaminants to which humans could be exposed under various salt cavern release scenarios and exposure pathways.

Toxicity assessment also provides an estimate of the relationship between the extent of exposure to a contaminant and the increased likelihood or severity of adverse effects. Dose-response evaluation is the process of evaluating, in a quantitative manner, the toxicity information and characterizing the relationship between the dose of the contaminant received and the incidence of adverse health effects in an exposed individual. Dose-response relationships provide toxicity values that are used to estimate the incidence or potential for adverse effects as a function of human exposure to the contaminant. Section 7.2 describes dose-response relationships for the contaminants of concern and provides toxicity values, where available, for each of those contaminants. These toxicity values are used in combination with contaminant intake information to estimate the potential for human health risks associated with salt cavern disposal of NOW.

7.1 Hazard Identification

Typically, two categories of toxicity are addressed in human health risk assessments: carcinogenic and noncarcinogenic. Carcinogens are believed to act via a "nonthreshold" mechanism of action; that is, a risk would be associated with any exposure level, no matter how small. Noncarcinogens are believed to act via a "threshold" mechanism of action; that is, there is some level of exposure (the threshold) below which the contaminant is unlikely to have an effect.

The following paragraphs describe the hazards associated with the contaminants of concern identified in the previous sections (i.e., arsenic, benzene, cadmium, and chromium). As noted in Section 4, contaminants such as boron and lead would form insoluble precipitates and would not migrate to areas where they could come in contact with humans. The information presented comes from the Agency for Toxic Substances and Disease Registry (ATSDR) Fact Sheets. These fact sheets are available on the Internet and summarize information about various hazardous substances, including their health effects (ATSDR 1993).

Arsenic. Arsenic is a metal usually found in compounds with oxygen, chlorine, sulfur, carbon, or hydrogen. Some arsenic compounds can dissolve in water. Arsenic can change from one form to another, but it does not break down. Exposure comes from ingesting contaminated water, soil, or air. Other exposure routes include breathing workplace air or burning smoke from wood containing arsenic. High levels (60 ppm [mg/L]) in food or water can be fatal; lower levels can cause nausea, decreased production of blood cells, and abnormal heart rhythms. Arsenic is a

known carcinogen; ingesting inorganic arsenic increases the risk of skin cancer and tumors of the bladder, kidney, liver, and lung. The EPA has set a limit of 0.05 ppm for arsenic in drinking water (EPA 1994a).

Benzene. Benzene is a colorless liquid with a sweet odor that is found in crude oil and gasoline. In liquid form, benzene mixes easily in water. In water, benzene can change quickly into a vapor and mix readily with the air. In air, it reacts with other chemicals and breaks down within a few days. It can move from soil to groundwater. Plants and animals do not store high levels of benzene. The most common exposure route is inhalation, but benzene can also be ingested. Most exposure comes from tobacco smoke, auto exhaust, and industrial emissions. Benzene is a known human carcinogen and is associated with leukemia. EPA has set a maximum permissible level of benzene in drinking water of five parts per billion (ppb) (5×10^{-9}) per day for a lifetime of exposure. The EPA has set a goal of 0 ppb for drinking water and rivers and lakes. The maximum permissible level of benzene in water for children for short-term exposures (10 days) is 235 ppb.

Cadmium. Cadmium is found naturally in the earth's crust. It is usually combined with other elements (e.g., oxygen, chlorine, sulfur), and it has no definite taste or odor. Cadmium binds strongly to soil particles, and some cadmium dissolves in water. It can change form in the environment but does not break down. Cadmium can accumulate in the human body from many years of low-level exposure. Exposure comes from eating foods that contain cadmium and drinking contaminated water. Other sources include breathing contaminated workplace air, cigarette smoke, or air near the burning of fossil fuels or municipal waste. On the basis of weak evidence of lung cancer in humans from breathing cadmium and strong evidence from animal studies, cadmium and cadmium compounds may be reasonably anticipated to cause cancer in humans. It is not known whether cadmium causes cancer from eating or drinking contaminated food or water. The EPA has set a limit of 5 ppb for cadmium in drinking water.

Chromium. Chromium occurs naturally in rocks, soils, plants, and animals. It has three main forms. These are chromium 0, which does not occur naturally; chromium III, the compounds of which are stable and occur naturally; and chromium VI, which rarely occurs. Chromium III is an essential nutrient in the human diet, but only small amounts are needed. Chromium adheres strongly to soil particles, but small amounts of chromium move from soil to groundwater. In surface water, most chromium sticks to dirt particles that settle to the bottom; only a small amount dissolves. Human exposure comes from ingestion or inhalation, especially breathing contaminated workplace air or sawdust from chromium-treated wood. At high levels, all forms of chromium can be toxic, but chromium VI is more toxic than chromium III. Long-term exposure to high or moderate levels of chromium VI can damage the nose and lungs. Ingesting large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and death. Certain chromium VI compounds are known carcinogens. ATSDR has insufficient data to determine if chromium 0 or chromium III are carcinogens. The EPA has set an MCL for total chromium of 0.1 mg/L.

7.2 Dose-Response Relationships for Contaminants of Concern

Toxicity values are used to translate a dose of a contaminant (the intake) into a risk for cancer or a hazard index for noncancer effects. There are two types of toxicity values: slope factors and reference doses. Section 7.2.1 describes slope factors for the contaminants of concern; Section 7.2.2 describes reference doses for the contaminants of concern.

7.2.1 Slope Factors

Slope factors are used to estimate the toxicities of carcinogens. A slope factor is defined as a plausible upper-bound estimate of the probability of a response per unit intake of a chemical over a lifetime. It is used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime of exposure to a particular level of a potential carcinogen. A curve representing the response per unit intake for a given chemical is known as a dose-response curve. This curve is developed by evaluating toxicity information and characterizing the relationship between the dose of a contaminant received and the incidence of adverse health effects.

Dose-response curves and slope factors are developed for various exposure routes (e.g., oral, inhalation). Because the potential exposure pathways identified for salt cavern release modes is always ingestion of groundwater, the oral slope factor is used. The slope factor is the upper 95% confidence limit of the slope of the dose-response curve. Because it represents the upper 95% confidence limit of the slope of the curve and because the slope is determined using very conservative models, the slope factor itself is conservative. As a result, the risks calculated using slope factors tend to be upper-bound estimates of the "true" risks. The oral slope factors for the contaminants of concern come from EPA's Integrated Risk Information System (IRIS) and are shown in Table 7-1.

7.2.2 Reference Doses

Reference doses (RfD) are used to estimate the toxicities of noncarcinogens. An RfD is an estimate of the "safe dose" of a contaminant for humans. A variety of RfDs are available, depending on the exposure route (e.g., oral, inhalation), the critical effect (e.g., developmental) and the length of exposure being evaluated (e.g., chronic [long time] event, or acute [a single, short-time event]). Because the only potential exposure pathway to humans for salt caverns is ingestion of groundwater, only the oral RfDs are used in calculating noncarcinogenic hazards. RfDs are conservative because EPA applies order-of-magnitude safety factors to allow for uncertainty. As a result, the hazards estimated using RfDs tend to be upper-bound estimates of the "true" hazards. RfDs for the contaminants of concern come from IRIS and are listed in Table 7-2.

Often the data needed to develop toxicity values are weak or unavailable; typically, data from animal studies are extrapolated to human studies. Also, a number of uncertainties are associated with the models used to derive toxicity values, and safety factors are incorporated into the derivation of toxicity factors. Because EPA continually reviews and revises its toxicity

values, they may change over time. Toxicity values provide the major source of uncertainty in risk assessments.

8. Risk Characterization

Human health risks from contaminants at waste disposal caverns may be carcinogenic or noncarcinogenic. This section describes these two types of risks and uses the information derived from Section 6 on exposure pathways and exposure-point concentrations and the toxicity values described in Section 7 to develop risk estimates for the contaminants of concern. Section 8.1 reviews the information developed in Section 6 to produce exposure-point concentrations for the release scenarios. Section 8.2 describes potential cancer risks from those scenarios, and Section 8.3 describes their potential noncancer risks.

8.1 Exposure Scenarios

Section 6 described the potential release modes. These were (1) failure of the cavern seal, resulting in contaminated fluid entering the groundwater at the depth of the cavern or at more shallow depths; (2) release of contaminated fluid through a crack in the salt; (3) release of contaminated fluid through a leaky interbed or higher permeability nonhomogeneous zone; and (4) a partial cavern roof fall, resulting in the release of contaminated fluids to deep or shallow groundwater. For all of the release modes, the exposure pathway would be ingestion of contaminated groundwater by residents living near the salt caverns. Table 8.1 summarizes the potential release modes.

The concentrations of the contaminants reaching the water that humans may drink depend on the location of the release, i.e., release to a shallow aquifer or release to a deep aquifer (see Table 6-2). Exposure-point concentrations are the concentrations of the contaminants in groundwater (shallow or deep) at the point of contact with a human receptor. Estimated exposure-point concentrations derived in Section 6 for the contaminants of concern are summarized in Tables 8-2 through 8-7. Note that in estimating the exposure-point concentrations, assumptions were made about the probability that the release event would actually occur. Thus, the concentrations in Section 6 were calculated assuming that the release would occur. These concentrations need to be adjusted for the likelihood of actual occurrence. Tables 8-2 through 8-7 show the exposure-point concentrations assuming release occurs, the probability that the release would occur based on the discussion in Section 6.2.6, and the resulting exposure-point concentrations used for estimating risk. Note that the exposure-point concentrations for benzene would be zero for all scenarios because of biodegradation along the flow path.

To estimate the amount of contaminant actually received from drinking contaminated water, assumptions must be made regarding time, frequency, and duration of exposure to that water. These assumptions are presented in Table 8-7. Unless otherwise indicated, standard EPA default exposure factors are used in the assumptions (EPA 1991).

Using these assumptions and the exposure-point concentrations, an intake rate for each contaminant of concern can be calculated with the following equation:

$$I_i = \frac{C_i \times IR \times ET \times EF \times ED \times CF}{BW \times AT} \quad (5)$$

where

- I_i = Intake of contaminant I
- C_i = Exposure point concentration of contaminant I , in g/L
- IR = Intake rate in L/day
- ET = Exposure time, in h/d
- EF = Exposure frequency in d/yr
- ED = Exposure duration, in yr
- CF = Conversion factor of 1 d/24 h
- BW = Body weight of the receptor, in kg, and
- AT = Averaging time, in d (for carcinogens, AT = 25,550 d (70 years); for noncarcinogens, AT = 365 d/y x ED)

Tables 8-9 through 8-14 show the intake rates in milligrams per kilogram-day for each contaminant of concern for the release scenarios for best-estimate and worst-case conditions.

8.2 Cancer Risks

Cancer risk is the likelihood of getting cancer. It is expressed as a probability (e.g., 1 in 100,000, which equals 10^{-5}). A 10^{-5} risk is a one-in-one hundred thousand excess risk of cancer from a given level of exposure to a particular contaminant. In other words, each individual exposed to that contaminant at that level over his/her lifetime has a one-in-one-hundred-thousand chance of getting cancer from that particular exposure. Cancer risk is described as excess because it is above the existing background risk of cancer. (In a population of one million people, the number of background cancer cases is roughly between 250,000 and 333,000.) An alternative interpretation is that one additional case of cancer would be expected to occur in a population of one million people who are all exposed under the same circumstances to a particular contaminant.

Cancer risks were calculated for each contaminant and for each exposure route for that contaminant and were then summed over all contaminants and exposure routes. Because the only exposure pathway for potential contaminant releases from a disposal cavern would be groundwater, the only exposure route is ingestion.

Human cancer risks associated with disposal of nonhazardous oil-field wastes in salt caverns are estimated for the release scenarios using the following equation:

$$R_i = I_i \times SF_i \quad (6)$$

where

- R_i = Risk from contaminant I,
- I_i = Intake of contaminant I, and
- Sf_i = Slope factor for contaminant I.

Using Equation 6 and the data in Tables 8-9 through 8-14 (intake estimates) and Table 7-1 (oral slope factors), cancer risks were estimated for each of the individual contaminants for the release scenarios for best-estimate and worst-case conditions. The results are presented in Tables 8-15 and 8-16. The total cancer risk for the release scenarios is the sum of the individual cancer risks for all contaminants of concern. Because there are no slope factors available for cadmium and chromium, and the exposure-point concentration of benzene would be 0.0 for all of the release scenarios, the total cancer risk is thus equal to the risk estimate for arsenic.

For worst-case conditions, the total cancer risks range from 2.0×10^{-17} for failure of the cavern seal with a fluid release at the depth of the cavern and for cracks releasing fluid at the depth of the cavern to 1.1×10^{-8} for a release scenario in which there is a partial roof fall and cavern seal failure with a failed casing at a shallow depth that releases contaminated fluid to the shallow aquifer (Table 8-16). Even under worst-case conditions, the excess cancer risks would lie well below the acceptable target risk range (1×10^{-4} to 1×10^{-6}) of the EPA that was established for remedial action goals for National Priority List (NPL) sites (40 CFR300.430(e)(2)(I)(A)(2)). For best-estimate conditions, the estimated cancer risks would be less (Table 8-15). For best-estimate conditions, the estimated cancer risks would be less.

8.3 Noncancer Risks

Risks associated with noncarcinogens are expressed as hazard quotients, which is the intake of a particular contaminant divided by its RfD. Because the RfD is the estimated "safe" dose for humans, when a hazard quotient exceeds 1, there is a potential for adverse noncarcinogenic effects. Hazard quotients are not probabilities. A hazard quotient that is less than one indicates a very low potential for noncarcinogenic effects. A hazard quotient that is greater than one indicates that the information on the exposure should be reviewed to determine the significance of the finding. Like carcinogenic risks, hazard quotients are summed over contaminants and exposure routes. However, for salt caverns, the only exposure route would be the oral pathway (ingestion of groundwater). Also, hazard quotients for multiple contaminants may not be strictly additive because different chemicals may affect different organs.

For a single contaminant, I , the hazard quotient is calculated according to the equation,

$$HQ_i = \frac{I_i}{RfD_i} \quad (7)$$

where

Hq_i = Hazard quotient from contaminant I,

I_i = Intake of contaminant I, and

RfD_i = Reference dose for contaminant I.

Using Equation 7 and the data in Tables 8-9 through 8-14 (intake estimates) and Table 7-2 (oral RfD s), noncancer risks are estimated for each of the individual contaminants for the release scenarios for both best-estimate and worst-case conditions. The results are shown in Tables 8-17 and 8-18. All of the contaminants of concern would have hazard quotients that are much less than one. Even when the hazard quotients are summed for all contaminants in a given release scenario, the greatest hazard index (sum of the individual hazard quotients) under worst-case conditions would be 6×10^{-5} , which is much less than one (Table 8-18). For best-estimate conditions, the largest total hazard index would be less (1.4×10^{-5}) (Table 8-17).

9. Sensitivity of Risks to Operating Procedures and Regulatory Structures

The risk estimates calculated in Section 8 indicate that the potential for human health risks associated with disposal of nonhazardous oil field wastes in salt caverns is very low. These risks were estimated assuming normal operating conditions and standard operating procedures for cavern closure. Any relaxation in design, monitoring, or operating practices could increase these risks.

At the same time, because the projected risks from failure of the cavern seal or cavern walls are low, the results of this preliminary assessment would not appear to support the imposition of additional safety regulations (i.e., regulations beyond those assumed to be used under normal operational and post-operational conditions). For example, the health risks estimated for release of contaminants into a deep or shallow aquifer assume that the residents who drink the water would be at a lateral distance of 1,000 ft from the edge of the disposal cavern. Risks would be lower if the population drinking the water were further away. Therefore, based on the estimates of cancer and noncancer risks presented in Section 8, it would not be necessary to implement any new requirements for residents living in the vicinity of waste caverns.

Although the risks associated with spills, accidents, and equipment leaks during normal operations were not evaluated in this study, it is likely that contaminants released from such occurrences would present greater risks than those derived from the cavern itself. Consequently, care should be taken to ensure that operating practices continue to be monitored in a way that minimizes the occurrence of surface accidents.

10. Summary

This report investigated the potential for human health risks associated with the use of salt caverns for nonhazardous oil-field waste disposal. Based on assumptions that were developed for a generic cavern and generic oil-field wastes, the estimated human health risks for worst-case conditions are very low (excess cancer risks of between 1.1×10^{-8} and 2.0×10^{-17}) and hazard indices (referring to noncancer health effects) of between 6×10^{-5} and 1.0×10^{-7} . Normally, risk managers consider risks of 1×10^{-6} and less and hazard indices of less than 1 to be acceptable. For best-estimate conditions, the excess cancer risks and hazard indices would be less.

Because these risks were developed for a hypothetical cavern, and site-specific conditions related to cavern type, location, and characteristics of the waste being disposed will vary, it would be prudent to conduct a site-specific risk assessment for an actual cavern, perhaps for an existing cavern currently in use for waste disposal. Such an assessment would provide a more realistic and useful assessment than the generic one described in this report.

A few comments on the use of the results of this report are in order. First, the assessment does not address risks to workers at the cavern disposal site. Such risks would be comparable to or less than worker risks associated with hydrocarbon cavern storage operations. (Because of the potential for explosions at hydrocarbon storage operations, worker risks for nonhazardous oil-field waste disposal may be less than for hydrocarbon storage.) Second, the assessment does not determine whether any health effects will occur in the future; it only estimates cancer risk and potential for noncarcinogenic effects. Third, risks have only been estimated for contaminants for which toxicity values were available; just because there is no toxicity value does not mean there is no risk. Finally, the assessment is limited to human health effects produced by nonradioactive contamination; it does not address the possible ecological risks associated with salt cavern disposal, nor does it estimate risks associated with NORM that may be included in oil field wastes.

11. References

Adriano, D.C., 1986, *Trace Elements in the Terrestrial Environment*, Springer-Verlag, New York.

Agency for Toxic Substances and Disease Registry, 1989, "Toxicological Profile for Chromium," ATSDR/TP-88/10, prepared by Syracuse Research Corporation for Toxic Substances and Disease Registry, U.S. Public Health Service, July.

Agency for Toxic Substances and Disease Registry, 1990, "Draft Toxicological Profile for Boron," prepared by Life Systems, Inc., for Toxic Substances and Disease Registry, U.S. Public Health Service, October.

Agency for Toxic Substances and Disease Registry, 1993, ToxFAQs fact sheets, available from the Internet at <http://atsdr1.atsdr.cdc.gov:8080/tfacts2.html>.

API, 1994, "Design of Solution-Mined Underground Storage Practices," API Recommended Practice 1114, American Petroleum Institute, Washington, D.C., June.

ATSDR = see Agency for Toxic Substances and Disease Registry.

Back, W., J.S. Rosenshein, and P.R. Seaber, 1988, *The Geology of North America*, Volume O-2, The Geological Society of America, Inc., Boulder, Colorado, 524p.

Baes, C.F., and R.D. Sharp, 1983, "A Proposal for Estimation of Soil Leaching and Leaching Constants for Use in Assessment Models," *Journal of Environmental Quality*, 12(1):17-28.

Baes, C.F., et al., 1984, "A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides through Agriculture," ORNL-5786, prepared by Oak Ridge National Laboratory, Oak Ridge, Tennessee, for the U.S. Department of Energy, Oak Ridge Operations, Oak Ridge, Tennessee.

Bair, E.S., 1987, "Analysis of Hydraulic Gradients Across the Host Rock at the Proposed Texas Panhandle Nuclear-Waste Repository Site," *Ground Water*, 25(4):440-447.

Bair, E.S., T.P.O. O'Donnell, and L.W. Picking, 1985, Potentiometric Mapping from Incomplete Drill-Stem Test Data: Palo Duro Basin Area, Texas and New Mexico.

Baker, D.E., and M.C. Amacher, 1982, Nickel, Copper, Zinc, and Cadmium, in *Methods of Soil Analysis*, Part 2: Chemical and Microbiological Properties, Second Edition, A.L. Page et al. (editors), American Society of Agronomy, Inc., Madison, Wisconsin.

Bassett, R.L., and M.E. Bentley, 1982, "Geochemistry and Hydrodynamics of Deep Formation Brines in the Palo Duro and Dalhart Basins, Texas, U.S.A.," *Journal of Hydrology*, 59:331-372.

Berest, P., and B. Brouard, 1995, "Behavior of Sealed Solution-Mined Caverns," presented at the Spring Meeting of the Solution Mining Research Institute, New Orleans, Louisiana, April.

Berest, P., B. Brouard, J. Bergues, J. Frelat, and G. Durup, 1997a, "Salt Caverns and the Compressibility Factor," presented at the Fall Meeting of the Solution Mining Research Institute, El Paso, Texas, October.

Berest, P., B. Brouard, F. Beugin, and J. Goldberg, 1997b, "Storage of Tritiated Water in Salt Caverns," presented at the Fall Meeting of the Solution Mining Research Institute, El Paso, Texas, October.

Biringer, K.L., 1984, "Strategic Petroleum Reserve Cavern, Geotechnical Data Base," SAND84-1500, Sandia National Laboratories, Albuquerque, New Mexico.

Bishop, W.M., 1986, "Long-Term Disposition of SPR Caverns Not Used for Petroleum Storage, A Draft Plan," unpublished report, employed by PB-KBB, Houston, TX, October.

Bradley, H.B., 1992, *Petroleum Engineering Handbook*, Society of Petroleum Engineers, Richardson, Texas.

Brown, B., and O. Helmer, 1964, "Improving the Reliability of Estimates Obtained from a Consensus of Experts," P-2986, The RAND Corporation.

Callahan, M.A., et al., 1979, "Water-Related Environmental Fate of 129 Priority Pollutants," EPA 440/4-79-029A, Office of Water Planning and Standards, Washington, D.C.

Capuano, R.M., and R.Z. Jan, 1996, "In-Situ Hydraulic Conductivity of Clay and Silt-Clay Fluvial-Deltaic Sediments, Texas Gulf Coast," *Ground Water*, 34(3):545-551.

CRC, 1968, *Handbook of Chemistry and Physics*, The Chemical Rubber Company, Cleveland, Ohio.

Chilingarian, G.V., J.O. Robertson, Jr., and S. Kumar, 1989, *Surface Operations in Petroleum Production, II*, Elsevier, New York, 562p.

EPA: see U.S. Environmental Protection Agency.

Freeze, R.A., and J.A. Cherry, 1979, *Groundwater*, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 604p.

Freeze, G.A., K.W. Larson, P.B. Davies, and S.W. Webb, 1995, "Using a Multiphase Flow Code to Model the Coupled Effects of Repository Consolidation and Multiphase Brine and Gas Flow at the Waste Isolation Pilot Plant," AICHE Heat Transfer Symposium, Portland, Oregon, E.L. Gaden, Jr., Series Editor, Volume 91, Number 306, American Institute of Chemical Engineers, New York.

Hanor, J.S., 1993, "Effective Hydraulic Conductivity of Fractured Clay Beds at a Hazardous Waste Landfill, Louisiana Gulf Coast," *Water Resources Research*, 29 (11): 3691-3698.

Hern, S.C., and S.M. Melancon, 1987, *Vadose Zone Modeling of Organic Pollutants*, Lewis Publishers, Chelsea, Michigan, 295p.

Hickerson, R., 1995, "Oilfield Waste Disposal in a Salt Cavern," in Proceedings of the Annual Underground Injection Control and Ground Water Protection Forum, Kansas City, Missouri, October.

Howard, P.H., R.S. Boethling, W.F. Jarvis, W.M. Meylan, and E.M. Michalenko, 1991, *Handbook of Environmental Degradation Rates*, Lewis Publishers, Inc., Chelsea, Michigan, 225p.

Lallemand-Barres, A., and P. Peaudecerf, 1978, "Recherche des Relations Entre la Valeur de la Dispersivite Macroscopique d'un Milieu Aquifere, Ses Autres Caracteristiques et les Conditions de Mesure," *Bulletin Bureau Geologique Minieres*, Sect. 3, Vol. 4, p277-284.

Langer, M., M. Wallner, and H. Wassman, 1984, "Gebirgsmechanische Bearbeitung von Stabilatsfragen bei Deponiekavernen im Salzgebirge" (Geoengineering with Respect to Stability of Cavities Used for Disposal Purposes, in German), *Kali und Steinsalz*, 2, p66-76.

Linn, J., 1997, personal communication, February.

Lu, P.Y., et al., 1975, "Model Ecosystem Studies of Lead and Cadmium and of Urban Sewage Sludge Containing These Elements," *Journal of Environmental Quality*, 4:505-509.

Lyman, W.J., P.J. Reidy, and B. Levy, 1992, *Mobility and Degradation of Organic Contaminants in Subsurface Environments*, C.K. Smoley, Inc., Chelsea, Michigan, 395p.

Mackay, D., W.Y. Shiu, and K.C. Ma, 1992, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Volume 1, Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs*, Lewis Publishers, Chelsea, Michigan, 697p.

Maidment, D.R., 1993, *Handbook of Hydrology*, McGraw-Hill, Inc., New York.

Makridakis, S., and R.L. Winkler, 1983, "Averages of Forecasts: Some Empirical Results," *Management Science*, 29(9):987-996.

Montgomery, J.H., 1991, *Groundwater Chemicals Desk Reference Volume 2*, Lewis Publishers, Chelsea, Michigan, 944p.

Montgomery, J.H., and L.M. Welkom, 1991, *Groundwater Chemicals Desk Reference*, Lewis Publishers, Chelsea, Michigan, 640p.

Pfeifle, T.W., T.J. Vogt, and G.A. Brekken, 1995, "Correlation of Chemical, Mineralogic, and Physical Characteristics of Gulf Coast Dome Salt to Deformation and Strength Properties," Solution Mining Research Institute Research Project Report 94-0004-S, January.

Postgate, J.K., 1965, "Recent Advances in the Study of Sulfate-Reducing Bacteria," *Bacteriological Reviews*, 29(4):December.

Querio, C.W., 1980, "Design and Construction of Solution-Mined Caverns for LPG Storage," presented at the Fall Meeting of the Solution Mining Research Institute, Minneapolis, Minnesota, October.

Radian Corporation, 1995, "Risk Assessment of Converting Salt Caverns to Natural Gas Storage, Final Report," GRI-95/0377, prepared for the Gas Research Institute, Austin, Texas, October.

Rai, D., J.M. Zachara, A.P. Schwab, et al., 1986, "Chemical Attenuation Rates, Coefficients, and Constants in Leachate Migration, Volume 1," A Critical Review, Report to Electric Power Research Institute, Palo Alto, California by Battelle, Pacific Northwest Laboratories, Richland, Washington, Research Project 2198-1.

Reisenauer, H.M., 1982, "Chromium," in *Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties*, Second Edition, A.L. Page et al. (editors), American Society of Agronomy, Inc., Madison, Wisconsin.

Richey, S.F., J.G. Wells, and K.T. Stephens, 1985, "Geohydrology of the Delaware Basin and Vicinity, Texas and New Mexico," U.S. Geological Survey, Water Resources Investigations Report 84-4077, Albuquerque, New Mexico.

SAIC, 1994, "Statistical Analysis of Effluent from Coastal Oil and Gas Extraction Facilities," prepared by Science Applications International Corporation, Falls Church, Virginia, for U.S. Environmental Protection Agency, Office of Science and Technology, September 30.

Seni, S.J., 1980, "Sand-Body Geometry and Depositional Systems, Ogallalla Formation, Texas," The University of Texas at Austin, Bureau of Economic Geology Report of Investigation No. 5, Austin, Texas, 35p.

Sheppard, M.I., D.I. Beals, D.H. Thibault, and P. O'Connor, 1984, "Soil Nuclide Distribution Coefficients and Their Statistical Distributions," AECL-8364, Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Limited, Pinawa, Manitoba, December.

SMRI: see Solution Mining Research Institute.

Solution Mining Research Institute (SMRI), 1997, Letter to J. Veil, Argonne National Laboratory, August 6.

Stanier, R.Y., et al., 1963, *The Microbial World*, Second Edition, Prentice Hall, Englewood Cliffs, New Jersey.

Streeter, V.L., 1961, *Handbook of Fluid Dynamics*, McGraw-Hill Book Company, Inc., New York.

Stumm, W., and J.J. Morgan, 1981, *Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters*, John Wiley and Sons, New York, 780p.

Testa, S.A., 1994, *Geological Aspects of Hazardous Waste Management*, CRC Press, Boca Raton, Florida, 537p.

Tomasko, D., 1985, "A Numerical Model for Predicting the Thermal Behavior of Caverns in the Strategic Petroleum Reserve," Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, the University of New Mexico, Albuquerque, New Mexico.

Tomasko, D., 1991, "Modeling Vertical and Horizontal Solute Transport," American Geophysical Union Fall Meeting, San Francisco, California, December.

Tomasko, D., 1994, "An Analytical Model for LNAPL Transport in the Vadose Zone," Geological Society of America Fall Meeting, Seattle, Washington, December.

U.S. Department of Energy, 1990, "Final Supplemental Environmental Impact Statement Waste Isolation Pilot Plant," DOE/EIS-0026-FS, Office of Environmental Restoration and Waste Management, January.

U.S. Department of Energy, 1996, "Workshop on Managing Human Health and Ecological Risk Assessment Projects under CERCLA and RCRA," Office of Environment Safety and Health, prepared by Argonne National Laboratory, May.

U.S. Environmental Protection Agency, 1987, "Report to Congress, Management of Wastes from the Exploration, Development, and Production of Crude Oil, Natural Gas, and Geothermal Energy, Volume 1 of 3," EPA/530-SW-88-003, Office of Solid Waste and Emergency Response, Washington, D.C., December.

U.S. Environmental Protection Agency, 1989, "Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual (Part A)," EPA/540/1-89/002, Office of Emergency and Remedial Response, December.

U.S. Environmental Protection Agency, 1991, "Human Health Evaluation Manual, Supplemental Guidance: Standard Default Exposure Factors," OSWER Directive 9285.6-03, Office of Solid Waste and Emergency Response, Washington, D.C., March 25.

U.S. Environmental Protection Agency, 1993, "Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Offshore Subcategory of the Oil and

Gas Extraction Point Source Category," EPA 821-R-93-003, Office of Water, Washington, D.C., January.

U.S. Environmental Protection Agency, 1994a, "Drinking Water Regulations and Health Advisories," Office of Water, Washington, D.C., May.

U.S. Environmental Protection Agency, 1994b, "Associated Waste Report: Crude Oil Tank Bottoms and Oily Debris," Office of Solid Waste, Special Waste Branch, Washington, D.C., March.

Van Sambeek, L. L., 1993, "Evaluating Cavern Tests and Subsurface Subsidence Using Simple Numerical Models," presented at the 7th Symposium on Salt, Vol. I.

Veil, J., D. Elcock, M. Raivel, D. Caudle, R.C. Ayers, Jr., and B. Grunewald, 1996, "Preliminary Technical and Legal Evaluation of Disposing of Nonhazardous Oil Field Waste into Salt Caverns," prepared for the U.S. Department of Energy, Office of Fossil Energy under contract W-31-109-ENG-38, Argonne National Laboratory, Argonne, Illinois, June.

Wallner, M., 1986, "Frac-Pressure Risk in Rock Salt," presented at the Fall Meeting of the Solution Mining Research Institute, Amsterdam.

Wallner, M., and W.A. Paar, 1997, "Risk of Progressive Pressure Build Up in a Sealed Cavern," presented at the Fall Meeting of the Solution Mining Research Institute, El Paso, Texas, October.

Werner, M.L., 1986, "Structure and Mineralization of the Richton Dome Caprock Boring MRIG-9 Technical Report," BMI/ONWI-610, Office of Nuclear Waste Isolation, Columbus, Ohio.

Whiting, G.H., 1981a, "Strategic Petroleum Reserve (SPR) Geologic Site Characterization Report, Sulphur Mines Salt Dome," SAND80-7141, Sandia National Laboratories, Albuquerque, New Mexico, March.

Whiting, G.H., 1981b, "Strategic Petroleum Reserve (SPR) Geologic Site Characterization Report, West Hackberry Salt Dome," SAND80-7131, Sandia National Laboratories, Albuquerque, New Mexico, January.

Williams, T.A., and A.K. Williamson, 1989, "Estimating Water-Table Altitudes for Regional Ground-Water Flow Modeling, U.S. Gulf Coast," *Ground Water*. 27(3):333-340.

Windholz, M., S. Budavari, R.F. Blumetti, and E.S. Otterbein, 1983, *The Merck Index, An Encyclopedia of Chemicals, Drugs, and Biologicals*, Merck & Company, Rahway, New Jersey.

Winkler, R.L., 1968, "The Consensus of Subjective Probability Distributions," *Management Science*, 15(2): B-61—B-75.

Winkler, R.L., 1977, "The Consensus of Subjective Probability Forecasts: Are Two, Three, ... Heads Better Than One?," Fifth Conference on Probability and Statistics, Las Vegas, Nevada, November.

Winkler, R.L., and R.T. Clemen, 1992, "Sensitivity of Weights in Combining Forecasts," Technical Notes, *Operations Research*, 40(3):609-614.

Winkler, R.L., and R.K. Sarin, 1981, "Risk Assessment: Consulting the Experts," *The Environmental Professional*, 3:265-276.

Wood, W.W., and W.E. Sanford, 1995, "Chemical and Isotopic Methods for Quantifying Ground-Water Recharge in a Regional, Semiarid Environment," *Ground Water*, 33(3):458-468.

Tables

(Note: Numbers presented in these tables have been rounded)

Table 6-1 Chemical Constituent Concentrations Assumed for Cavern Brine at the Time of Release

Type of Waste/Reference	Concentration Range (mg/L unless otherwise noted)			
	Benzene	Arsenic	Cadmium	Chromium
Produced water				
SAIC (1994)	0.08-14	BDL ^a -0.032	BDL-0.098	BDL-0.85
EPA (1993) ^b	0.052-20.4	0.017-0.31	0.0012-0.098	--
EPA (1987) ^b	0.47-2.9	0.02-1.7	--	--
Drilling Waste				
EPA (1987) ^b TCLP data ^c	-- ^d	BDL-0.002	0.011-0.29	BDL-0.78
EPA (1987) ^a analysis of waste itself	-- ^d	BDL-0.01 mg/kg	2 - 5.4 mg/kg	22-190 mg/kg
Tank Bottoms				
EPA (1994b) TCLP data	BDL-13	BDL-0.06	BDL- 0.008	BDL-0.14
EPA (1994b) analysis of waste itself	0.175-2,686 mg/kg	0.47-166 mg/kg	0.32-6,500 mg/kg	1.7-1,170 mg/kg
Selected Concentrations ^e	20.4	1.7	0.29	0.85

^a BDL = value is below detection limit.

^b Range is from the median to the upper 90th percentile.

^c TCLP = toxicity characteristic leaching procedure.

^d No data reported in this reference.

^e Highest value for each constituent in TCLP samples for produced water, drilling waste, and tank bottoms.

Table 6-2 Summary Table of Release Calculations

Release Scenario	Contaminant	Retardation	Initial Conc. (mg/L)	Concentration at 1,000 yrs (mg/L) ^a	Concentration at 1,000 yrs (mg/L) ^b	MCL (mg/L)
Cavern seal fails and releases fluid at depth	Benzene	10	20.4	0.0		0.005
	Cadmium	50	0.29	4.1×10^{-8}		0.005
	Arsenic	200	1.7	9.5×10^{-15}		0.05
	Chromium	500	0.85	7.7×10^{-15}		0.1
Cavern seal fails and releases fluid to shallow aquifer	Benzene	10	20.4	0.0		0.005
	Cadmium	50	0.29	1.0×10^{-6c}		0.005
	Arsenic	200	1.7	1.2×10^{-5}		0.05
	Chromium	500	0.85	1.2×10^{-8}		0.1

Table 6.2 Summary Table of Failure Calculations (continued)

Release Scenario	Contaminant	Retardation	Initial Conc. (mg/L)	Concentration at 1,000 yrs (mg/L) ^a	Concentration at 1,000 yrs (mg/L) ^b	MCL (mg/L)
Release from crack	Benzene	10	20.4	0.0		0.005
	Cadmium	50	0.29	4.1×10^{-8}		0.005
	Arsenic	200	1.7	9.5×10^{-15}		0.05
	Chromium	500	0.85	7.7×10^{-15}		0.1
Release from leaky interbed	Benzene	10	20.4		0.0	0.005
	Cadmium	50	0.29		1.6×10^{-8}	0.005
	Arsenic	200	1.7		6.1×10^{-13}	0.05
	Chromium	500	0.85		5.2×10^{-13}	0.1
Roof fall + release at depth	Benzene	10	20.4	0.0		0.005
	Cadmium	50	0.29	4.1×10^{-8}		0.005
	Arsenic	200	1.7	9.5×10^{-15}		0.05
	Chromium	500	0.85	7.7×10^{-15}		0.1

Table 6.2 Summary Table of Failure Calculations (continued)

Release Scenario	Contaminant	Retardation	Initial Conc. (mg/L)	Concentration at 1,000 yrs (mg/L) ^a	Concentration at 1,000 yrs (mg/L) ^b	MCL (mg/L)
Roof fall + cavern seal failure + release at depth	Benzene	10	20.4	0.0		0.005
	Cadmium	50	0.29	4.1×10^{-8}		0.005
	Arsenic	200	1.7	9.5×10^{-15}		0.05
	Chromium	500	0.85	7.7×10^{-15}		0.1
Roof fall + cavern seal failure + release at shallow depth	Benzene	10	20.4	0.0		0.005
	Cadmium	50	0.29	1.0×10^{-6c}		0.005
	Arsenic	200	1.7	1.2×10^{-5}		0.05
	Chromium	500	0.85	1.2×10^{-8}		0.1
Roof fall + release through leaky interbed	Benzene	10	20.4		0.0	
	Cadmium	50	0.29		1.6×10^{-8}	0.005
	Arsenic	200	1.7		6.1×10^{-13}	0.05
	Chromium	500	0.85		5.2×10^{-13}	0.1

^a Short, pulsed release.^b Long, slow release.^c Maximum concentration of 1.3×10^{-5} occurs at 334 yrs.

Table 6-3 Probabilities of Occurrence for Specified Release Scenarios

Release Scenario	No. of Responses	Best Estimate	Range	Worst Case	Range
Seal fails and releases fluid at depth	5	0.031	0.0005 to 0.1	0.12	0.002 to 0.25
Seal fails and releases fluid at shallow depth	5	0.012	0.0001 to 0.05	0.040	0.001 to 0.10
Cracks release fluid at depth	5	0.022	0.0001 to 0.10	0.120	0.001 to 0.35
Leaky interbeds release fluid at depth	5	0.022	0.0001 to 0.10	0.120	0.001 to 0.35
Roof fall plus fluid released at depth	5	0.100	10^{-6} to 0.50	0.290	10^{-5} to 1.0
Roof fall plus cavern seal fails and releases fluid at depth	5	0.062	5×10^{-6} to 0.2	0.163	2×10^{-5} to 0.35
Roof fall plus cavern seal fails and releases fluid at shallow depth	5	0.006	1×10^{-7} to 0.02	0.051	1×10^{-6} to 0.10
Roof fall plus release through leaky interbed	5	0.062	5×10^{-6} to 0.20	0.163	2×10^{-5} to 0.35

Table 7-1 Oral Slope Factors for Contaminants of Concern

Contaminant of Concern	Oral Slope Factor (1/ (mg/kg-day))
Arsenic	1.5
Benzene	0.029
Cadmium	NA
Chromium	NA

NA = Not available

Table 7-2 Oral Reference Doses for Contaminants of Concern

Contaminant of Concern	Oral RfD (mg/kg/day)
Arsenic	0.0003
Benzene	NA
Cadmium	0.0005
Chromium (III)	1.0
Chromium (VI)	0.005

NA = Not available

Table 8-1 Scenarios for Risk Calculations

Release Location	Release Modes
Release to shallow aquifer	<ul style="list-style-type: none"> - Cavern seal failure with casing failure at shallow depth - Cavern roof fall with cavern seal failure and casing failure at shallow depth
Release to deep aquifer	<ul style="list-style-type: none"> - Cavern seal failure with casing failure at depth of cavern - Cracks - Leaky interbeds - Roof fall with intact cavern seal - Roof fall with cavern seal failure and casing failure at depth of cavern - Roof fall with release through exposed leaky interbed

Table 8-2 Exposure-Point Concentrations for Deep, Best-Estimate Aquifer Release Scenarios

Contaminant	Conc. at 1,000 yr (mg/L)	Best-Estimate Probability of Occurrence					Best-Estimate Exposure-Point Concentrations (mg/L)			
		Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall + fluid released at depth	Roof fall + seal fails and fluid released at depth	Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall + fluid released at depth	Roof fall + seal fails and fluid released at depth	
Benzene	0.0	0.031	0.022	0.1	0.062	0.0	0.0	0.0	0.0	
Cadmium	4.1×10^{-8}	0.031	0.022	0.1	0.062	1.3×10^{-9}	9.0×10^{-10}	4.1×10^{-9}	2.5×10^{-9}	
Arsenic	9.5×10^{-15}	0.031	0.022	0.1	0.062	3.0×10^{-16}	2.1×10^{-16}	9.5×10^{-16}	5.9×10^{-16}	
Chromium	7.7×10^{-15}	0.031	0.022	0.1	0.062	2.4×10^{-16}	1.7×10^{-16}	7.7×10^{-16}	4.8×10^{-16}	

Table 8-3 Exposure-Point Concentrations for Deep, Worst-Case Aquifer Release Scenarios

Contaminant	Conc. at 1,000 yr (mg/L)	Worst-Case Probability of Occurrence				Worst-Case Exposure-Point Concentrations (mg/L)			
		Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall + fluid released at depth	Roof fall + seal fails and fluid released at depth	Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall + fluid released at depth	Roof fall + seal fails and fluid released at depth
Benzene	0.0	0.120	0.120	0.290	0.163	0.0	0.0	0.0	0.0
Cadmium	4.1×10^{-8}	0.120	0.120	0.290	0.163	4.9×10^{-9}	4.9×10^{-9}	1.2×10^{-8}	6.7×10^{-9}
Arsenic	9.5×10^{-15}	0.120	0.120	0.290	0.163	1.1×10^{-15}	1.1×10^{-15}	2.8×10^{-15}	1.6×10^{-15}
Chromium	7.7×10^{-15}	0.120	0.120	0.290	0.163	9.2×10^{-16}	9.2×10^{-16}	2.2×10^{-15}	1.3×10^{-15}

Table 8-4 Exposure-Point Concentrations for Shallow, Best-Estimate Aquifer Release Scenarios

Contaminant	Conc. at 1,000 yr (mg/L)	Best-Estimate Probability of Occurrence		Best-Estimate Exposure-Point Concentrations (mg/L)	
		Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails, + casing fails and releases fluid to shallow aquifer	Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails + casing fails and releases fluid to shallow aquifer
Benzene	0.0	0.012	0.006	0.0	0.0
Cadmium	1.0×10^{-6}	0.012	0.006	1.2×10^{-8a}	6.0×10^{-9}
Arsenic	1.2×10^{-5}	0.012	0.006	1.4×10^{-7}	7.2×10^{-8}
Chromium	1.2×10^{-8}	0.012	0.006	1.4×10^{-10}	7.2×10^{-11}

^a Maximum concentration of 1.6×10^{-7} mg/L occurs at 334 years.

Table 8-5 Exposure-Point Concentrations for Shallow, Worst-Case Aquifer Release Scenarios

Contaminant	Conc. at 1,000 yr (mg/L)	Worst-Case Probability of Occurrence		Worst-Case Exposure-Point Concentrations (mg/L)	
		Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails + casing fails and releases fluid to shallow aquifer	Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails + casing fails and releases fluid to shallow aquifer
Benzene	0.0	0.040	0.051	0.0	0.0
Cadmium	1.0×10^{-6}	0.040	0.051	4.0×10^{-8a}	5.1×10^{-8}
Arsenic	1.2×10^{-5}	0.040	0.051	4.8×10^{-7}	6.1×10^{-7}
Chromium	1.2×10^{-8}	0.040	0.051	4.8×10^{-10}	6.1×10^{-10}

^a Maximum concentration of 5.2×10^{-7} mg/L occurs at 334 years.

Table 8-6 Exposure-Point Concentrations for Additional Best-Estimate Releases at Depth

Contaminant	Conc. at 1,000 yr (mg/L)	Best-Estimate Probability of Occurrence		Best-Estimate Exposure- Point Concentrations (mg/L)	
		Leaky interbed releases fluid at depth	Roof fall + long slow release through leaky interbed at depth	Leaky interbed releases fluid at depth	Roof fall + release through leaky interbed at depth
Benzene	0.0	0.022	0.062	0.0	0.0
Cadmium	1.6×10^{-8}	0.022	0.062	3.5×10^{-10}	9.9×10^{-10}
Arsenic	6.1×10^{-13}	0.022	0.062	1.3×10^{-14}	3.8×10^{-14}
Chromium	5.2×10^{-13}	0.022	0.062	1.1×10^{-14}	3.2×10^{-14}

Table 8-7 Exposure-Point Concentrations for Additional Worst-Case Releases at Depth

Contaminant	Conc. at 1,000 yr (mg/L)	Worst-Case Probability of Occurrence		Worst-Case Exposure-Point Concentrations (mg/L)	
		Leaky interbed releases fluid at depth	Roof fall + long slow release through leaky interbed at depth	Leaky interbed releases fluid at depth	Roof fall + release through leaky interbed at depth
Benzene	0.0	0.120	0.163	0.0	0.0
Cadmium	1.6×10^{-8}	0.120	0.163	1.9×10^{-9}	2.6×10^{-9}
Arsenic	6.1×10^{-13}	0.120	0.163	7.3×10^{-14}	9.9×10^{-14}
Chromium	5.2×10^{-13}	0.120	0.163	6.2×10^{-14}	8.5×10^{-14}

Table 8-8 Exposure Scenario Assumptions for Ingestion of Groundwater

Parameter	Value
Daily intake rate	2 L/d
Exposure time	24 h/d
Exposure frequency ^a	350 d/yr
Exposure duration ^a	30 yr
Body weight of human receptor	70 kg
Averaging time	
Carcinogens (70 yr)	25,550 d
Noncarcinogens (365 d/yr × ED) ^b	10,950 d

^a Exposure frequency and exposure duration based on specifics of failure mode.

^b ED = exposure duration.

Table 8-9 Estimated Intake Rates for Deep, Best-Estimate Aquifer Release Scenarios

	Intake Rate (mg/kg-day)									
	Seal fails and releases fluid at depth		Crack releases fluid at depth		Roof fall and fluid released at depth		Roof fall plus seal fails and fluid released at depth			
Contaminant	Carcinogen	Non-carcinogen	Carcinogen	Non-carcinogen	Carcinogen	Non-carcinogen	Carcinogen	Non-carcinogen	Carcinogen	Non-carcinogen
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cadmium	1.6×10^{-11}	3.5×10^{-11}	1.1×10^{-11}	2.4×10^{-11}	4.9×10^{-11}	1.1×10^{-10}	3.0×10^{-11}	6.8×10^{-11}		
Arsenic	3.6×10^{-18}	8.1×10^{-18}	2.5×10^{-18}	5.7×10^{-18}	1.1×10^{-17}	2.6×10^{-17}	7.1×10^{-18}	1.6×10^{-17}		
Chromium	2.9×10^{-18}	6.5×10^{-18}	2.0×10^{-18}	4.6×10^{-18}	9.2×10^{-18}	2.1×10^{-17}	5.8×10^{-18}	1.3×10^{-17}		

Table 8-10 Estimated Intake Rates for Deep, Worst-Case Aquifer Release Scenarios

	Intake Rate (mg/kg-day)							
	Seal fails and releases fluid at depth		Crack releases fluid at depth		Roof fall and fluid released at depth		Roof fall plus seal fails and fluid released at depth	
	Carcinogen	Non-carcinogen	Carcinogen	Non-carcinogen	Carcinogen	Non-carcinogen	Carcinogen	Non-carcinogen
Contaminant								
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cadmium	5.9×10^{-11}	1.3×10^{-10}	5.9×10^{-11}	1.3×10^{-10}	1.4×10^{-10}	3.2×10^{-10}	8.0×10^{-11}	1.8×10^{-10}
Arsenic	1.3×10^{-17}	3.0×10^{-17}	1.3×10^{-17}	3.0×10^{-17}	3.4×10^{-17}	7.6×10^{-17}	1.9×10^{-17}	4.3×10^{-17}
Chromium	1.1×10^{-17}	2.5×10^{-17}	1.1×10^{-17}	2.5×10^{-17}	2.6×10^{-17}	5.9×10^{-17}	1.6×10^{-17}	3.5×10^{-17}

Table 8-11 Estimated Intake Rates for Shallow, Best-Estimate Aquifer Release Scenarios

	Intake Rate (mg/kg-day)			
	Seal fails, casing fails, and fluid released to shallow aquifer		Roof fall + seal fails + casing fails and releases fluid to shallow aquifer	
	Carcinogen	Noncarcinogen	Carcinogen	Noncarcinogen
Benzene	0.0	0.0	0.0	0.0
Cadmium	1.4×10^{-10a}	3.2×10^{-10b}	7.2×10^{-11}	1.6×10^{-10}
Arsenic	1.7×10^{-9}	3.8×10^{-9}	8.6×10^{-10}	1.9×10^{-9}
Chromium	1.7×10^{-12}	3.8×10^{-12}	8.6×10^{-13}	1.9×10^{-12}

^a Maximum concentration of 1.9×10^{-9} mg/kg-day occurs at 334 years.

^b Maximum concentration of 4.2×10^{-9} mg/kg-day occurs at 334 years.

Table 8-12 Estimated Intake Rates for Shallow, Worst-Case Aquifer Release Scenarios

	Intake Rate (mg/kg-day)			
	Seal fails, casing fails, and fluid released to shallow aquifer		Roof fall + seal fails + casing fails and releases fluid to shallow aquifer	
	Carcinogen	Noncarcinogen	Carcinogen	Noncarcinogen
Benzene	0.0	0.0	0.0	0.0
Cadmium	4.8×10^{-10a}	1.1×10^{-9b}	6.1×10^{-10}	1.4×10^{-9}
Arsenic	5.8×10^{-9}	1.3×10^{-8}	7.3×10^{-9}	1.7×10^{-8}
Chromium	5.8×10^{-12}	1.3×10^{-11}	7.3×10^{-12}	1.7×10^{-11}

^a Maximum concentration of 6.2×10^{-9} mg/kg-day occurs at 334 years.

^b Maximum concentration of 1.4×10^{-8} mg/kg-day occurs at 334 years.

Table 8-13 Estimated Intake Rates for Additional, Best-Estimate Aquifer Release Scenarios

	Intake Rate (mg/kg-day)			
	Leaky interbed releases fluid at depth		Roof fall + release thorough leaky interbed at depth	
	Carcinogen	Noncarcinogen	Carcinogen	Noncarcinogen
Contaminant				
Benzene	0.0	0.0	0.0	0.0
Cadmium	4.2×10^{-12}	9.5×10^{-12}	1.2×10^{-11}	2.7×10^{-11}
Arsenic	1.6×10^{-16}	3.5×10^{-16}	4.6×10^{-16}	1.0×10^{-15}
Chromium	1.3×10^{-16}	3.0×10^{-16}	3.8×10^{-16}	8.6×10^{-16}

Table 8-14 Estimated Intake Rates for Additional, Worst-Case Aquifer Release Scenarios

	Intake Rate (mg/kg-day)			
	Leaky interbed releases fluid at depth		Roof fall + release through leaky interbed at depth	
	Carcinogen	Noncarcinogen	Carcinogen	Noncarcinogen
Contaminant				
Benzene	0.0	0.0	0.0	0.0
Cadmium	2.3×10^{-11}	5.1×10^{-11}	3.1×10^{-11}	7.0×10^{-11}
Arsenic	8.8×10^{-16}	2.0×10^{-15}	1.2×10^{-15}	2.7×10^{-15}
Chromium	7.4×10^{-16}	1.7×10^{-15}	1.0×10^{-15}	2.3×10^{-15}

Table 8-15 Estimated Cancer Risks for Best-Estimate Aquifer Release Scenarios

Contaminant	Release Scenario							
	Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall and fluid released at depth	Roof fall plus seal fails and fluid released at depth	Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails + casing fails and releases fluid to shallow aquifer	Leaky interbed releases fluid at depth	Roof fall + release through leaky interbed at depth
Arsenic	5.4×10^{-18}	3.8×10^{-18}	1.7×10^{-17}	1.1×10^{-17}	2.6×10^{-9}	1.3×10^{-9}	2.4×10^{-16}	6.9×10^{-16}
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cadmium	NA	NA	NA	NA	NA	NA	NA	NA
Chromium III	NA	NA	NA	NA	NA	NA	NA	NA
Chromium VI	NA	NA	NA	NA	NA	NA	NA	NA
Total	5.4×10^{-18}	3.8×10^{-18}	1.7×10^{-17}	1.1×10^{-17}	2.6×10^{-9}	1.3×10^{-9}	2.4×10^{-16}	6.9×10^{-16}

NA = Not available

Table 8-16 Estimated Cancer Risks for Worst-Case Aquifer Release Scenarios

Contaminant	Release Scenario							
	Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall and fluid released at depth	Roof fall plus seal fails and fluid released at depth	Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails + casing fails and releases fluid to shallow aquifer	Leaky interbed releases fluid at depth	Roof fall + release through leaky interbed at depth
Arsenic	2.0×10^{-17}	2.0×10^{-17}	5.1×10^{-17}	2.9×10^{-17}	8.7×10^{-9}	1.1×10^{-8}	1.3×10^{-15}	1.8×10^{-15}
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cadmium	NA	NA	NA	NA	NA	NA	NA	NA
Chromium III	NA	NA	NA	NA	NA	NA	NA	NA
Chromium VI	NA	NA	NA	NA	NA	NA	NA	NA
Total	2.0×10^{-17}	2.0×10^{-17}	5.1×10^{-17}	2.9×10^{-17}	8.7×10^{-9}	1.1×10^{-8}	1.3×10^{-15}	1.8×10^{-15}

NA = Not available

Table 8-17 Estimated Noncancer Risks for Best-Estimate Aquifer Release Scenarios

Contaminant	Release Scenario							
	Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall and fluid released at depth	Roof fall plus seal fails and fluid released at depth	Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails + casing fails and releases fluid to shallow aquifer	Leaky interbed releases fluid at depth	Roof fall + release through leaky interbed at depth
Arsenic	2.7×10^{-14}	1.9×10^{-14}	8.7×10^{-14}	5.3×10^{-14}	1.3×10^{-5}	6.3×10^{-6}	1.2×10^{-12}	3.3×10^{-12}
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cadmium	7.0×10^{-8}	4.8×10^{-8}	2.2×10^{-7}	1.4×10^{-7}	6.4×10^{-7a}	3.2×10^{-7}	1.9×10^{-8}	5.4×10^{-8}
Chromium III	6.5×10^{-18}	4.6×10^{-18}	2.1×10^{-17}	1.3×10^{-17}	3.8×10^{-12}	1.9×10^{-12}	3.0×10^{-16}	8.6×10^{-16}
Chromium VI	1.3×10^{-15}	9.2×10^{-16}	4.2×10^{-15}	2.6×10^{-15}	7.6×10^{-10}	3.8×10^{-10}	6.0×10^{-14}	1.7×10^{-13}
Total	7.0×10^{-8}	4.8×10^{-8}	2.2×10^{-7}	1.4×10^{-7}	1.4×10^{-5}	6.6×10^{-6}	1.9×10^{-8}	5.4×10^{-8}

^a 8.4×10^{-6} Maximum concentration occurs at 334 years.

Table 8-18 Estimated Noncancer Risks for Worst-Case Aquifer Release Scenarios

Contaminant	Release Scenario							
	Seal fails and releases fluid at depth	Crack releases fluid at depth	Roof fall and fluid released at depth	Roof fall plus seal fails and fluid released at depth	Seal fails, casing fails, and fluid released to shallow aquifer	Roof fall + seal fails + casing fails and releases fluid to shallow aquifer	Leaky interbed releases fluid at depth	Roof fall + release through leaky interbed at depth
Arsenic	1.0×10^{-13}	1.0×10^{-13}	2.5×10^{-13}	1.4×10^{-13}	4.3×10^{-5}	5.7×10^{-5}	6.7×10^{-12}	9.0×10^{-12}
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cadmium	2.6×10^{-7}	2.6×10^{-7}	6.4×10^{-7}	3.6×10^{-7}	2.2×10^{-6a}	2.8×10^{-6}	1.0×10^{-7}	1.4×10^{-7}
Chromium III	2.5×10^{-17}	2.5×10^{-17}	5.9×10^{-17}	3.5×10^{-17}	1.3×10^{-11}	1.7×10^{-11}	1.7×10^{-15}	2.3×10^{-15}
Chromium VI	5.0×10^{-15}	5.0×10^{-15}	1.2×10^{-14}	7.0×10^{-15}	2.6×10^{-9}	3.4×10^{-9}	3.4×10^{-13}	4.6×10^{-13}
Total	2.6×10^{-7}	2.6×10^{-7}	6.4×10^{-7}	3.6×10^{-7}	$4.5 \times 10^{-5*}$	6.0×10^{-5}	1.0×10^{-7}	1.4×10^{-7}

^a Maximum concentration of 2.8×10^{-5} occurs at 334 years.

Radiological Dose Assessment of NORM Disposal in Class II Injection Wells*

Karen P. Smith, Gustavious P. Williams, Deborah L. Blunt, John J. Arnish
Environmental Assessment Division
Argonne National Laboratory

ABSTRACT

Subsurface disposal of petroleum industry wastes containing naturally occurring radioactive material (NORM) via injection into Class II wells was modeled to estimate potential radiological doses to individuals consuming water from a shallow aquifer. A generic model was developed for the injection of 100,000 barrels of NORM waste containing 2,000 picocuries per liter of radium into a layered geologic system. In separate modeling runs, it was assumed that a casing failure released the entire volume of NORM into each successive geologic layer, including the shallow aquifer. Radionuclide concentrations and related potential doses were calculated for receptors located in the shallow aquifer from 0 to 20 miles downgradient of the injection well. The results indicated that even under conservative assumptions, calculated radionuclide concentrations and potential doses associated with subsurface disposal of NORM in Class II wells were below levels of regulatory concern. The preliminary results from a dose assessment of a specific project entailing injection of NORM into Class II wells support the conclusions of the generic study.

INTRODUCTION

In the past few years, the petroleum industry has adopted methods for managing and disposing of waste streams containing naturally occurring radioactive material (NORM) that are more restrictive than past practices and are likely to provide greater isolation of radioactivity. Simultaneously, many states have promulgated regulations imposing stricter standards on the management of NORM wastes. The result of these actions has been increased costs of waste management for the petroleum industry.

* Funding for this work was provided by the U.S. Department of Energy, Office of Policy and Office of Fossil Energy, under contract W-31-109-Eng-38.

The U.S. Department of Energy (DOE) has funded a number of studies to assess the potential risks associated with various NORM disposal options, including the disposal of NORM by injection into existing, permitted Class II wells.* The results of these studies indicate that this form of disposal presents a negligible risk to the general public. In the first such study (1), potential doses resulting from underground injection of NORM were modeled by assuming a generic geologic setting. A subsequent study (2) modeled the potential doses resulting from injection of NORM into several, specific Class II injection wells that will be used for NORM disposal in a technology demonstration project. The results of these studies are presented in this paper. Greater detail regarding the methodologies, assumptions, and input parameters is contained in the referenced reports.

GENERIC STUDY

In the generic study of NORM disposal in a Class II well (1), underground injection was modeled by assuming a geologic setting of interlayered sandstone and shale deposits, the shallowest unit being a sandstone drinking water aquifer. A conservative set of assumptions was used. Separate model runs were made assuming that during injection, a casing failure caused the entire volume of NORM-contaminated waste to be injected into each geologic layer, in turn, including the drinking water aquifer. Radionuclide concentrations were calculated at a number of receptor locations in the drinking water aquifer, ranging from 0 to 20 miles (mi) downgradient from the injection site. SWIFT II (3), a three-dimensional model, was used to model the casing failures and subsequent transport of radionuclides to the downgradient receptor locations. Annual doses resulting from the radionuclide concentrations were calculated using exposure parameters recommended by the U.S. Environmental Protection Agency for maximum residential exposures (4).

Assumptions and Input Parameters

The stratigraphy modeled in the generic study consisted of six interlayered sandstone and shale units. The upper unit was assumed to be a 1,800-foot (ft) thick sandstone layer that served as a drinking water aquifer at the receptor locations. This unit was underlain by alternating shale and sandstone units, each 1,600 ft thick. The porosities of the sandstone and shale units were assumed to be 0.2 and 0.1, respectively. The units were tilted, with a slope of 0.01. The regional groundwater gradient also was assumed to

* Class II injection wells are a specific category of injection wells used by the oil and gas industry to dispose of saltwater produced in conjunction with oil or gas, to inject fluids to enhance oil recovery, or to store hydrocarbon liquids. Class II permitting requirements are established by the Underground Injection Control Program, Part C of the Safe Drinking Water Act of 1974.

be 0.01. This gradient is large but yields conservative estimates for travel times and concentrations in the model.

To calculate the source term for the generic study, it was assumed that 100,000 barrels (bbl) of a slurry containing NORM wastes with a radium concentration of 2,000 picocuries per liter (pCi/L) were injected over a period of four days. The exposure pathway assumed that casing failure during injection released the entire volume of NORM wastes into the subsurface units. Upon release, all of the radium dissolved instantaneously. The dissolved radium was transported in the subsurface to a drinking water well, and ingestion of contaminated groundwater resulted in exposure. To calculate potential doses, it was assumed that an individual consumed 2 liters of water per day for 350 days per year.

Casing failures were simulated at three different depths within the top sandstone aquifer: one at a shallow depth (300 ft), one at the midpoint (900 ft), and one near the bottom (1,500 ft). Failures also were simulated at the midpoint of each of the underlying units at depths of 2,600 ft (shale), 4,200 ft (sandstone), 5,800 ft (shale), 9,000 ft (sandstone), and 10,600 ft (shale). Receptor points were located at a depth of 300 ft within the sandstone aquifer at distances ranging from 0 mi (i.e., coincident with the injection well) to 20 mi downgradient.

The model was run first to calculate the radium-226 and radon-222 concentrations at each of the receptor points. Additional calculations were made by assuming two domestic wells were pumping simultaneously at a rate of 14,400 gallons per day (gal/day), 0.2 and 0.5 mi from the injection site, respectively. This rate was chosen as a reasonable rate for a domestic well in a sandstone aquifer. In addition, sensitivity analyses of some of the key input parameters were conducted to assess their impact on predicted doses. Parameters chosen for the sensitivity analyses included those for which a set of definitive values could not be chosen because of variability in possible conditions (e.g., groundwater gradient or hydraulic conductivity) and those for which definitive data have not been collected but are thought to be very variable (e.g., source term concentration).

Results

Table 1 lists the concentrations of radium-226 depths and the corresponding estimated doses calculated at the three closest receptor points for the three shallowest casing failures. All of the calculated concentrations were below the current maximum allowable concentration of total radium in drinking water of 5 pCi/L, established under the Safe Drinking Water Act (5). In addition, all of the estimated doses were well below the currently accepted general public dose limit of 100 millirem per year (mrem/yr) from all sources, recommended by the International Commission on Radiological Protection (6). All of the other model runs (i.e., scenarios in which failure occurred at a depth greater than 1,500 ft or runs in which the receptor was located more than 0.5 mi away) resulted in extremely low predicted radium concentrations, at least four orders of magnitude below those presented in Table 1. (The calculated radon-222 concentrations for all scenarios were at least four orders of magnitude below those calculated for radium-226. Because

these concentrations are considered to be insignificant, they are not presented in this paper.)

Receptor points at pumping wells located 0.2 and 0.5 mi downgradient had lower estimated doses because of plume dispersion. Increasing the hydraulic conductivity or gradient by one order of magnitude increased the estimated doses at the receptor points; however, the doses were still well below the currently accepted standard. Doubling the concentration of radium in the NORM slurry effectively doubled the estimated doses.

NORM DEMONSTRATION PROJECT

Through its Oil and Gas Environmental Program, the DOE is co-funding the demonstration of a new NORM treatment and disposal technology developed by BPF, Inc., that entails final disposal of the NORM via injection into Class II injection wells (7). The BPF technology is a mobile, modular system in which NORM wastes are treated and disposed of at the lease site where the NORM is stored. The technology entails dissolving the radionuclides into a liquid solution and injecting that solution back into subsurface formations, using existing permitted injection wells located on or near the lease site. The three main processes provided by the treatment modules are (1) deoiling, (2) volume reduction, and (3) radionuclide extraction. In the BPF process, the radionuclide extraction process consists of dissolving the NORM solids and segregating the dissolved NORM from insoluble material present in the waste stream. This process is accomplished in a series of treatment steps, including chemical dissolution, carbonate roasting, and solids separation. The liquid effluents containing dissolved radionuclides are disposed of in an injection well along with the produced water already being injected.

Evaluation of the BPF technology is underway; laboratory and bench-scale demonstrations have been conducted, and pilot-scale demonstrations at three field sites are expected to begin in the fall of 1997. At each of the three sites, an existing Class II injection well has been identified for the disposal of the radioactive effluents. During the pilot-scale field demonstrations, BPF expects to dispose of 840 to 2,100 gal/day of radioactive effluent. The activity level of the effluents is expected to range from 40,000 to 80,000 pCi/L of radium. The depths of injection for the identified wells range from 4,000 to 10,500 ft.

Assumptions and Input Parameters

To assist with the technology evaluation, a preliminary radiological dose assessment of the pilot-scale activities was conducted. The exposure pathway in this assessment assumed that casing failure would result in the release of the radioactive effluent at a shallower depth than intended, that the radionuclides would be transported to a drinking water well, and that an individual would ingest the contaminated water. Because the previous generic study indicated that casing failures below the drinking water

aquifer resulted in negligible doses, the model runs for the NORM demonstration project considered only direct releases into a drinking water aquifer, even though the Class II wells to be used inject at much greater depths.

As a worst-case scenario for all three sites, it was assumed that casing failure occurred at a depth of 100 ft in a shallow aquifer having a porosity of 0.2. Receptor points were located at a depth of 100 ft at distances of 100, 500, 1,000, and 5,000 ft from the injection well. It was assumed that 2,100 gal of effluent would be lost instantaneously; this volume represents the largest quantity expected to be handled in any given day during the demonstration project. The models were run for effluent activity levels of 40,000 and 80,000 pCi/L of radium.

Results

Table 2 lists the concentrations of radium-226 calculated at the receptor points and the corresponding estimated doses. As they were in the generic study, all of the calculated concentrations were below the current maximum allowable concentration of total radium in drinking water of 5 pCi/L (5), and all of the estimated doses were well below the currently accepted general public dose limit of 100 mrem/yr from all sources(6).

At least two factors characterizing the NORM demonstration project that were not accounted for in the preliminary dose assessment would result in lower estimated doses if they were addressed in the assumptions and input parameters. One factor is that during injection the radioactive effluent will be combined with a significant volume (up to 750,000 gal/day) of produced water that is already being injected into the Class II wells on a regular basis. This will result in significant dilution of the effluent activity levels. The other factor is that the nearest known pumping well to any of the three sites is approximately 0.5 mi away. This well serves a stock tank and is unlikely to produce water consumed by a human. The nearest possible drinking water well appears to be more than 5,000 ft away. Potential doses at distances greater than 5,000 ft will be negligible.

CONCLUSIONS

The results of the radiological dose assessments presented in this paper indicate that the subsurface disposal of NORM wastes via injection into permitted Class II wells presents only a negligible risk to the general public. In simulations of casing failures that release the radionuclides directly into a drinking water aquifer, radioactivity levels and associated radiological doses were predicted to be below levels of regulatory concern, even at nearby receptors. If more realistic assumptions regarding failure scenarios and receptor locations were used, potential doses would be negligible.

REFERENCES

1. Smith, K.P., et al., Radiological Dose Assessment Related to Management of Naturally Occurring Radioactive Materials Generated by the Petroleum Industry, ANL/EAD-2, Argonne, Illinois, Argonne National Laboratory (1996).
2. Blunt, D.L., et al., Risk Assessment for Bench-Scale Phase of the NORM Treatment and Disposal Demonstration Project, Argonne, Illinois, Argonne National Laboratory (1997).
3. Reeves, M., et al., Theory and Implementation for SWIFT II: The Sandia-Waste Isolation and Transport Model for Fractured Media, Release 4.84, NUREG/CR-3328, SAND83-119, Albuquerque, New Mexico, Sandia National Laboratory (1986).
4. U.S. Environmental Protection Agency, Risk Assessment Guidance for Superfund, Volume I: Human Health Evaluation Manual, Interim Final, EPA/540/R-92/003, Washington, D.C. (1991).
5. U.S. Environmental Protection Agency, "National Primary Drinking Water Regulations," *Code of Federal Regulations*, title 40, part 141.
6. International Commission on Radiological Protection, 1990 Recommendations of the International Commission on Radiological Protection, Publication No. 60, Oxford, U.K., Pergamon Press (1991).
7. Capone, D.W., "Results from Bench-Scale Testing of a Mobile NORM Treatment and Disposal System," presented at the Third International Petroleum Environmental Conference, Albuquerque, New Mexico (September 24-27, 1996).

Table 1. Estimated Activities and Potential Doses Associated with Subsurface Injection of 4.2 Million Gallons (100,000 barrels) of NORM in a Generic Setting.

Top Aquifer Failure Depth (ft)	Receptor Location Downgradient from Injection Well (miles)					
	0.0		0.2		0.5	
	Activity Level (pCi/L)	Annual Dose (mrem)	Activity Level (pCi/L)	Annual Dose (mrem)	Activity Level (pCi/L)	Annual Dose (mrem)
300	*	*	1.317	1.00	0.211	0.20
900	0.250	0.20	0.155	0.10	0.053	0.04
1,500	0.015	0.01	0.017	0.01	0.010	0.08

* No value calculated because receptor location is coincident with failure location.

Table 2. Estimated Activities and Potential Doses Associated with Subsurface Injection of 2,100 Gallons (50 barrels) of Radioactive Effluent during the NORM Demonstration Project.

Receptor Location Downgradient from Injection Well (ft)	Effluent Radioactivity Level (pCi/L)			
	40,000		80,000	
	Activity Level (pCi/L)	Annual Dose (mrem)	Activity Level (pCi/L)	Annual Dose (mrem)
100	1.940	1.500	3.870	3.000
500	0.173	0.100	0.346	0.300
1,000	0.061	0.050	0.122	0.090
5,000	0.005	0.004	0.011	0.008